

Fourth Edition

Plastics Technology Handbook

Plastics Engineering Series

Manas Chanda
Salil K. Roy



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Fourth Edition

Plastics Technology Handbook

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Preface

One of the fastest changing fields today is the field of plastics as new polymers are synthesized, new uses are found, and existing processes and products are modified and improved for ecological needs, better economics, and better values. A need has thus been felt to bring out a new edition of the *Plastics Technology Handbook*, as it has established itself over the years as an important source book of information on modern plastics. In this new edition, the organization and structure of the book have not been altered, but each chapter has been substantially revised by eliminating less timely material and adding more important and relevant material as well as new topics of interest in the light of recent advances and new developments. The much appreciated textbook-like approach of the earlier editions has been retained as it offers to the reader not only the factual information on processing methods, properties, and applications of myriad polymers and polymeric products but also better understanding aided by critical insights into their basic molecular nature and behavior.

[Chapter 1](#), titled “Characteristics of Polymers” presents a thorough, comprehensive and self-contained account of different aspects of polymers at the molecular level to ensure a fuller appreciation of the wide range of application potential of polymers and the methods that can be used to upgrade their performance. Starting with a brief account of the molecular make-up and structural features of macromolecules and a brief overview of their methods of production, Chapter 1 focuses on the relationships among polymer properties, chemical structures, and physical states of aggregation and explains the significance, role, and mechanism of action of stabilizing agents and other additives that make plastics more useful by overcoming some of their inherent weaknesses. The discussion is supported by citing examples of common industrial recipes to highlight the application of theory into practice. In the new edition, recent advances in supramolecular polymerization, flame retardancy, polymer-based nanomedicines and drug delivery, and the new concept of oxo-biodegradable polymers have been discussed.

What makes plastics the most versatile of all materials is the ease with which they can be given any desired shape and form. Molding and fabrication processes, however, vary depending on the type of polymers to be processed and the end products to be made. [Chapter 2](#), which deals with polymer fabrication processes for plastics, rubber and fiber, has been thoroughly revised in the new edition to include recent developments in the respective fields and a number of processes not covered in the previous edition. Particularly, the discussion on plastic foams and foam extrusion processes has been further broadened.

[Chapter 3](#) deals with plastics properties and testing. Properties are discussed under four main headings — mechanical, electrical, optical, and thermal. Besides the remarkable ease and scope of plastics fabrication, what gives plastics the dominant place among all materials is the wide range of properties inherent in plastics or imparted by various means. The chapter discusses the four major types of properties, giving theoretical derivations where necessary and providing explanations on molecular and structural basis. The latter part of the chapter deals with methods of testing and identification of plastics. Where standard test methods have been developed, these have been included. The principles of these tests

have been shown with schematic diagrams, and the properties measured have been indicated. Simple and handy chemical tests for identification of most of the common types of plastics have been described in a structured manner.

In this book, polymers have been broadly divided into two categories, namely, industrial polymers and polymers in special uses. The first group of polymers is those which are produced on very large, large, and relatively large scales, including the so-called engineering polymers that possess superior mechanical properties for engineering applications. [Chapter 4](#), which deals with industrial polymers, has been revised by adding more information with regard to processing and applications of the polymers. The section on polyblends in this chapter has been expanded to include the new emerging field of nanoblends.

Besides a handful of high-volume polymers like polyethylene, polypropylene, polystyrene, poly(vinyl chloride), polycarbonate, nylon, polyesters, etc., which are very visible in everyday life, there are hundreds of other polymers, polymer derivatives, and polymeric combinations that play special and often critical roles in diverse fields of human activities. [Chapter 5](#) describes such polymers. Some of these specialty polymers possess, inherently, one or more special or some unusual properties that make them indispensable for specific applications, while there are many other polymers that are tailor-made to meet specific and critical needs. For a systematic discussion, these polymers can be placed in different groups according to their properties and/or areas of uses, such as high-temperature and fire-resistant polymers, liquid crystal polymers, electroactive polymers, electrolytic polymers, photoresist polymers, ionic and ion-exchange polymers, packaging polymers, biodegradable polymers, adhesive polymers, and polymers in optical information storage. While discussions on all these groups of polymers in Chapter 5 of the earlier edition have now been revised and updated, the new edition also features a number of new topics focusing on recent developments in polymer synthesis and applications. These new additions include polymeric sensors, conductive fiber fillers, polymeric optical fibers, polymer electrolyte membranes, biodegradable polymer scaffolds, scavenger resins, permselective polymer membranes, hydrogels and smart polymers, dendritic polymers, shape memory polymers, polymers in microencapsulation, polymer nanocomposites, wood-polymer composites, and polymerization-filled composites.

Plastics recycling is now an important area of activity both in terms of research and practice, driven by environmental pressure as well as economic considerations. Although plastics recycling has been practiced for many years with emphasis on recycling of industrial scraps and homogeneous post-consumer plastics, the industry has now accepted the challenge of recycling heterogeneous plastics waste based on new technologies of separation and processing. [Chapter 6](#) on recycling of plastics has been revised in the new edition to provide a state-of-the-art account of the various methods of plastics recycling available, highlighting both their merits and deficiencies.

As we live in a plastics age, the diverse fields of plastics technology are also undergoing rapid changes both qualitatively and quantitatively with many newer applications of common polymers and specialty polymers coming to light. While there are continuous improvements in the established uses of polymers, new uses are being developed in such diverse areas as the automotive and aerospace industries, packaging, agriculture, horticulture, domestic and sports appliances, office equipment, communication, electronics and electrical technology, and biomedical applications. The last chapter ([Chapter 7](#)), titled “Trends in Polymer Applications,” presents a comprehensive overview of new developments in polymer uses in all these areas.

The stimulus to venture on to the fourth edition of *Plastics Technology Handbook* has come from the consistently excellent response and acceptance shown by readers ever since the publication of the first edition of the book in 1982. We are indebted to them. Among many people who contributed assistance to the making of this new edition, we wish to thank particularly Ms. B. G. Girija of the Department of Chemical Engineering, Indian Institute of Science, Bangalore for patiently making computer graphics of all new illustrations in the book, Dr. Amitava Sarkar of Kentucky University (USA) and Dr. Deepyaman Seth of University of Waterloo (Canada) for providing valuable literature inputs, and Dr. Ajay Karmarkar and Dr. S. K. Sharma, both of the Institute of Wood Science and Technology, Bangalore, for offering

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Characteristics of Polymers

1.1 What Is a Polymer?

A molecule has a group of atoms which have strong bonds among themselves but relatively weak bonds to adjacent molecules. Examples of small molecules are water (H_2O), methanol (CH_3OH), carbon dioxide, and so on. Polymers contain thousands to millions of atoms in a molecule which is large; they are also called macromolecules. Polymers are prepared by joining a large number of small molecules called monomers. Polymers can be thought of as big buildings, and monomers as the bricks that go into them.

Monomers are generally simple organic molecules containing a double bond or a minimum of two active functional groups. The presence of the double bond or active functional groups act as the driving force to add one monomer molecule upon the other repeatedly to make a polymer molecule. This process of transformation of monomer molecules to a polymer molecule is known as polymerization. For example, ethylene, the prototype monomer molecule, is very reactive because it has a double bond. Under the influence of heat, light, or chemical agents this bond becomes so activated that a chain reaction of self-addition of ethylene molecules is generated, resulting in the production of a high-molecular-weight material, almost identical in chemical composition to ethylene, known as polyethylene, the polymer of ethylene (Figure 1.1).

The difference in behavior between ordinary organic compounds and polymeric materials is due mainly to the large size and shape of polymer molecules. Common organic materials such as alcohol, ether, chloroform, sugar, and so on, consist of small molecules having molecular weights usually less than 1,000. The molecular weights of polymers, on the other hand, vary from 20,000 to hundreds of thousands.

The name polymer is derived from the Greek *poly* for many and *meros* for parts. A polymer molecule consists of a repetition of the unit called a *mer*. Mers are derived from monomers, which, as we have seen for ethylene, can link up or polymerize under certain conditions to form the polymer molecule. The number of mers, or more precisely the number of repetitions of the mer, in a polymer chain is called the degree of polymerization (DP). Since the minimum length or size of the molecule is not specified, a relatively small molecule composed of only, say, 3 mers might also be called a polymer. However, the term polymer is generally accepted to imply a molecule of large size (macromolecule). Accordingly, the lower-molecular-weight products with low DP should preferably be called oligomers (*oligo*=few) to distinguish them from polymers. Often the term high polymer is also used to emphasize that the polymer under consideration is of very high molecular weight.

Because of their large molecular size, polymers possess unique chemical and physical properties. These properties begin to appear when the polymer chain is of sufficient length—i.e., when the molecular weight exceeds a threshold value—and becomes more prominent as the size of the molecule increases. The dependence of the softening temperature of polyethylene on the degree of polymerization is shown

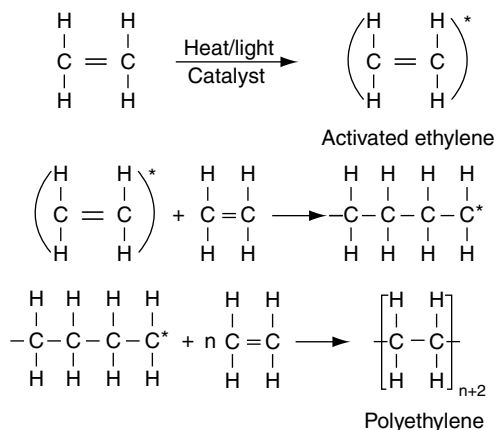


FIGURE 1.1 Intermediate steps during formation of polyethylene.

in Figure 1.2a. The dimer of ethylene is a gas, but oligomers with a DP of 3 or more (that is, C_6 or higher paraffins) are liquids, with the liquid viscosity increasing with the chain length. Polyethylenes with DP's of about 30 are greaselike, and those with DP's around 50 are waxes. As the DP value exceeds 400 or the molecular weight exceeds about 10,000, polyethylenes become hard resins with softening points about 100°C . The increase in softening point with chain length in the higher-molecular-weight range is small. The relationship of such polymer properties as tensile strength, impact strength, and melt viscosity with molecular weight is indicated in Figure 1.2b. Note that the strength properties increase rapidly first as the chain length increases and then level off, but the melt viscosity continues to increase rapidly. Polymers with very high molecular weights have superior mechanical properties but are difficult to process and fabricate due to their high melt viscosities. The range of molecular weights chosen for commercial polymers represents a compromise between maximum properties and processability.

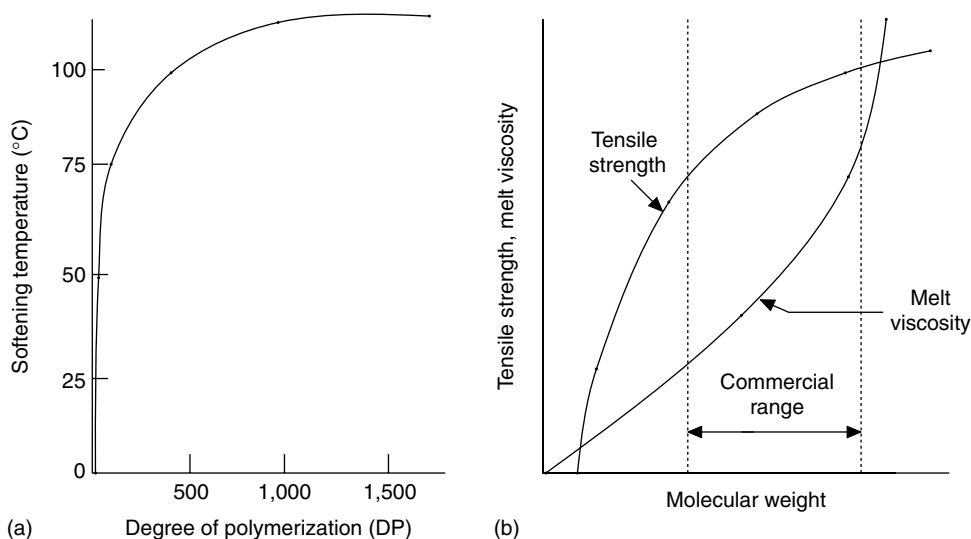


FIGURE 1.2 Polymer properties versus polymer size. (a) Softening temperature of polyethylene. (b) Tensile strength, and melt viscosity. (Adapted from Seymour, R. B. and Carraher, C. E. Jr., 1992. *Polymer Chemistry. An Introduction*. Marcel Dekker, New York.)

1.2 Molecular Weight of Polymers

In ordinary chemical compounds such as sucrose, all molecules are of the same size and therefore have identical molecular weights (M). Such compounds are said to be monodisperse. In contrast, most polymers are polydisperse. Thus a polymer does not contain molecules of the same size and, therefore, does not have a single molecular weight. In fact, a polymer contains a large number of molecules—some big, some small. Thus there exists a variation in molecular size and weight, known as *molecular-weight distribution* (MWD), in every polymeric system, and this MWD determines to a certain extent the general behavior of polymers. Since a polymer consists of molecules of different sizes and weights, it is necessary to calculate an average molecular weight (\bar{M}) or an *average degree of polymerization* (\overline{DP}).

The molecular weights commonly used in the characterization of a polydisperse polymer are the number average, weight average, and viscosity average.

Consider a sample of a polydisperse polymer of total weight W in which N =total number of moles; N_i =number of moles of species i (comprising molecules of the same size); n_i =mole fraction of species i ; W_i =weight of species i ; w_i =weight fraction of species i ; M_i =molecular weight of species i ; x_i =degree of polymerization of species i .

1.2.1 Number-Average Molecular Weight (\bar{M}_n)

From the definition of molecular weight as the weight of sample per mole, we obtain

$$\bar{M}_n = \frac{W}{N} = \frac{\sum N_i M_i}{N} = \sum n_i M_i \quad (1.1)$$

$$= \frac{\sum W_i}{\sum W_i / M_i} = \frac{\sum w_i}{\sum w_i / M_i} = \frac{1}{\sum w_i / M_i} \quad (1.2)$$

Dividing \bar{M}_n by the mer weight M_0 , we obtain a number-average degree of polymerization, \overline{DP}_n , where

$$\overline{DP}_n = \frac{\bar{M}_n}{M_0} = \frac{\sum N_i x_i}{\sum N_i} \quad (1.3)$$

The quantity \bar{M}_n is obtained by end-group analysis or by measuring a colligative property such as elevation of boiling point, depression of freezing point, or osmotic pressure [1,2].

1.2.2 Weight-Average Molecular Weight (\bar{M}_w)

Equation 1.1 indicates that in the computation of \bar{M}_n , the molecular weight of each species is weighted by the mole fraction of that species. Similarly, in the computation of weight-average molecular weight the molecular weight of each species is weighted by the weight fraction of that species:

$$\bar{M}_w = \sum w_i M_i = \frac{\sum W_i M_i}{\sum W_i} \quad (1.4)$$

$$= \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (1.5)$$

The weight-average degree of polymerization, \overline{DP}_w , is obtained by dividing \bar{M}_w , by the mer weight:

$$\overline{DP}_w = \frac{\bar{M}_w}{M_0} = \frac{\sum W_i x_i}{\sum W_i} \quad (1.6)$$

\bar{M}_w can be determined by measuring light scattering of dilute polymer solution [3,4]. \bar{M}_w is always higher than \bar{M}_n . Thus for a polymer sample containing 50 mol% of a species of molecular weight 10,000 and 50 mol% of species of molecular weight 20,000, Equation 1.1 and Equation 1.5 give $\bar{M}_n = 0.5(10,000 + 20,000) = 15,000$ and $\bar{M}_w = [(10,000)^2 + (20,000)^2]/[10,000 + 20,000] = 17,000$.

1.2.3 Viscosity-Average Molecular Weight (\bar{M}_v)

The viscosity-average molecular weight is defined by the equation

$$\bar{M}_v = \left[\sum w_i M_i^a \right]^{1/a} = \left[\sum N_i M_i^{1+a} / \sum N_i M_i \right]^{1/a} \quad (1.7)$$

For $a=1$, $\bar{M}_v = \bar{M}_w$ and for $a=-1$, $\bar{M}_v = \bar{M}_n$. Thus, \bar{M}_v falls between \bar{M}_w and \bar{M}_n , and for many polymers it is 10%–20% below \bar{M}_w . \bar{M}_v is calculated from the intrinsic viscosity $[\eta]$ by the empirical relation

$$[\eta] = K \bar{M}_v^\alpha \quad (1.8)$$

where K and α are constants. $[\eta]$ is derived from viscosity measurements by extrapolation to “zero” concentration [5,6].

In correlating polymer properties (such as reactivity) which depend more on the number of molecules in the sample than on the sizes of the molecules, \bar{M}_n is a more useful parameter than \bar{M}_w or \bar{M}_v . Conversely, for correlating polymer properties (such as viscosity) which are more sensitive to the size of the polymer molecules, \bar{M}_w or \bar{M}_v is more useful.

Because it is easy to determine, *melt index* often is used instead of molecular weight in routing characterization of polymers. It is defined as the mass rate of polymer flow through a specified capillary under controlled conditions of temperature and pressure. The index can often be related empirically to some average molecular weight, depending on the specific polymer. A lower melt index indicates a higher molecular weight, and vice versa.

1.2.4 Polydispersity Index

The ratio of weight-average molecular weight to number-average molecular weight is called the dispersion or polydispersity index (I). It is a measure of the width of the molecular-weight distribution curve (Figure 1.3) and is used as such for characterization purposes. Normally I is between 1.5 and 2.5, but it may range to 15 or greater. The higher the value of I is, the Greater is the spread of the molecular-weight distribution of the polymer. For a monodisperse system (e.g., pure chemicals), $I=1$.

There is usually a molecular size for which a given polymer property will be optimum for a particular application. So a polymer sample containing the greatest number of molecules of that size will have the optimum property. Since samples with the same average molecular weight may possess different molecular-weight distributions, information regarding molecular-weight distribution is necessary for a proper choice of polymer for optimum performance. A variety of fractionation techniques, such as fractional precipitation, precipitation chromatography, and gel permeation chromatography (GPC), based on properties such as solubility and permeability, which vary with molecular weight, may be used for separating polymers of narrow size ranges.

Example 1

A sample of poly(vinyl chloride) is composed according to the following fractional distribution (Figure 1.3).

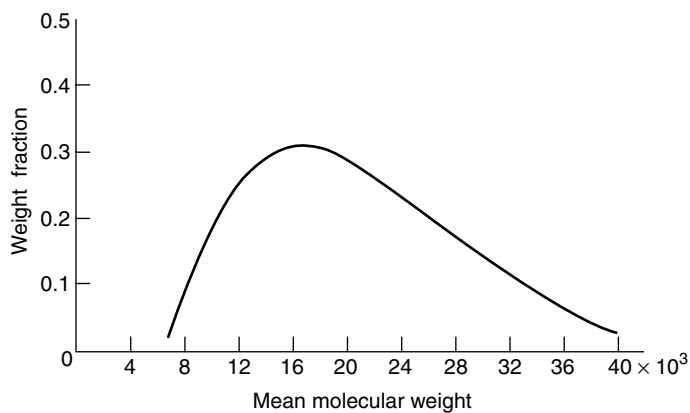


FIGURE 1.3 Molecular-weight distribution of a polymer.

Wt fraction	0.04	0.23	0.31	0.25	0.13	0.04
Mean mol. wt $\times 10^{-3}$	7	11	16	23	31	39

- (a) Compute \bar{M}_n , \bar{M}_w , \overline{DP}_n , and \overline{DP}_w .
 (b) How many molecules per gram are there in the polymer?

Answer. (a)

Wt fraction (w_i)	Mean mol. wt (M_i)	$w_i \times M_i$	w_i/M_i
0.04	7,000	280	0.57×10^{-5}
0.23	11,000	2,530	2.09×10^{-5}
0.31	16,000	4,960	1.94×10^{-5}
0.25	23,000	5,750	1.90×10^{-5}
0.13	31,000	4,030	0.42×10^{-5}
0.04	39,000	1,560	0.10×10^{-5}
Σ		19,110	6.21×10^{-5}

From Equation 1.2

$$\bar{M}_n = \frac{1}{6.21 \times 10^{-5}} = 16,100 \text{ g/mole}$$

From Equation 1.4

$$\bar{M}_w = 19,110 \text{ g/mole}$$

1 mer weight of vinyl chloride (C_2H_3Cl) = (2)(12) + (3)(1) + 35.5 = 62.5 g/mer

$$\overline{DP}_n = \frac{16,000 \text{ g/mole}}{62.5 \text{ g/mer}} = 258 \text{ mers/mole}$$

$$\overline{DP}_w = \frac{19,110 \text{ g/mole}}{62.5 \text{ g/mer}} = 306 \text{ mers/mole}$$

(b) Number of molecules per gram

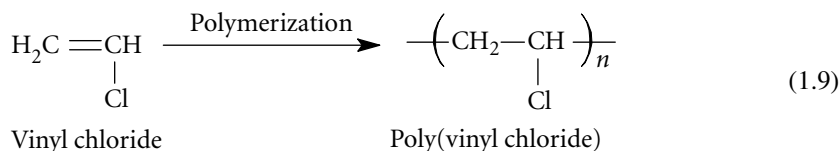
$$\begin{aligned} &= \sum \frac{w_i}{M_i} (\text{Avogadro number}) \\ &= (6.21 \times 10^{-5})(6.02 \times 10^{23}) \\ &= 3.74 \times 10^{19} \text{ molecules/g} \end{aligned}$$

1.3 Polymerization Processes

There are two fundamental polymerization mechanisms. Classically, they have been differentiated as addition polymerization and condensation polymerization. In the addition process, no by-product is evolved, as in the polymerization of vinyl chloride (see below); whereas in the condensation process, just as in various condensation reactions (e.g., esterification, etherification, amidation, etc.) of organic chemistry, a low-molecular-weight by-product (e.g., H₂O, HCl, etc.) is evolved. Polymers formed by addition polymerization do so by the successive addition of unsaturated monomer units in a chain reaction promoted by the active center. Therefore, addition polymerization is called chain polymerization. Similarly, condensation polymerization is referred to as step polymerization since the polymers in this case are formed by stepwise, intermolecular condensation of reactive groups. Another polymerization process that has now appeared as a new research area of considerable interest is supramolecular polymerization (see later).

1.3.1 Addition or Chain Polymerization

In chain polymerization, a simple, low-molecular-weight molecule possessing a double bond, referred to in this context as a monomer, is treated so that the double bond opens up and the resulting free valences join with those of other molecules to form a polymer chain. For example, vinyl chloride polymerizes to poly(vinyl chloride):



It is evident that no side products are formed; consequently the composition of the mer or repeating unit of the polymer (–CH₂–CHCl–) is identical to that of the monomer (CH₂=CHCl). The identical composition of the repeating unit of a polymer and its monomer(s) is, in most cases, an indication that the polymer is an addition polymer formed by chain polymerization process. The common addition polymers and the monomers from which they are produced are shown in [Table 1.1](#).

Chain polymerization involves three processes: chain initiation, chain propagation, and chain termination. (A fourth process, chain transfer, may also be involved, but it may be regarded as a combination of chain termination and chain initiation.) Chain initiation occurs by an attack on the monomer molecule by a free radical, a cation, or an anion; accordingly, the chain polymerization processes are called free-radical polymerization, cationic polymerization, or anionic polymerization. (In coordination addition or chain polymerization, described below separately, the chain initiation step is,

TABLE 1.1 Typical Addition Polymers (Homopolymers)

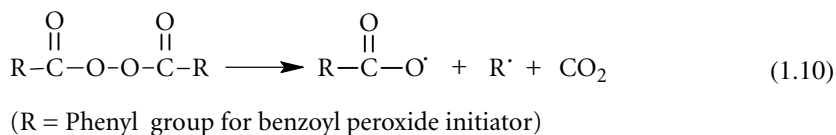
	Monomer	Polymer	Comments
1.	Ethylene $\text{CH}_2=\text{CH}_2$	Polyethylene (PE) $\text{—}(\text{CH}_2\text{—CH}_2)_n\text{—}$	High density polyethylene (HDPE) and low density polyethylene (LDPE); molded objects, tubing, film, electrical insulation, used for household products, insulators, pipes, toys, bottles, e.g., Alkathene, Lupolan, Hostalen, Marlex.
2.	Propylene $\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{CH}_3 \end{array}$	Polypropylene (PP) $\begin{array}{c} \text{—}(\text{CH}_2\text{—CH})_n\text{—} \\ \\ \text{CH}_3 \end{array}$	Lower density, stiffer, and higher temperature resistance than PE; used for water pipes, integral hinges, sterilizable hospital equipment, e.g., Propathene, Novolen, Moplen, Hostalen, Marlex.
3.	Styrene $\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array}$	Polystyrene (PS) $\begin{array}{c} \text{—}(\text{CH}_2\text{—CH})_n\text{—} \\ \\ \text{C}_6\text{H}_5 \end{array}$	Transparent and brittle; used for cheap molded objects, e.g., Styron, Carinex, Hostyren, Lustrex. Modified with rubber to improve toughness, e.g., High impact Polystyrene (HIPS) and acrylonitrile–butadiene–styrene copolymer (ABS). Expanded by volatilization of a blended blowing agent (e.g., pentane) to make polystyrene foam, e.g., Styrocell, Styrofoam
4.	Acrylonitrile $\text{H}_2\text{C}=\text{CH—CN}$	Polyacrylonitrile $\begin{array}{c} \text{—}(\text{CH}_2\text{—CH})_n\text{—} \\ \\ \text{CN} \end{array}$	Widely used as fibers; best alternative to wool for sweaters, e.g., Orlon, Acrilan.
5.	Vinylacetate $\begin{array}{c} \text{CH}_2=\text{CH—O—C—CH}_3 \\ \\ \text{O} \end{array}$	Poly(vinyl acetate) $\begin{array}{c} \text{—}(\text{CH}_2\text{—CH})_n\text{—} \\ \\ \text{O} \\ \\ \text{C=O} \\ \\ \text{CH}_3 \end{array}$	Emulsion paints, adhesives, sizing, chewing gum, e.g., Flovic, Mowilith, Mowicoll.
6.	Vinyl chloride $\text{CH}_2=\text{CH—Cl}$	Poly(vinyl chloride) (PVC) $\begin{array}{c} \text{—}(\text{CH}_2\text{—CH})_n\text{—} \\ \\ \text{Cl} \end{array}$	Water pipes, bottles, gramophone records, plasticized to make PVC film, leather cloth, raincoats, flexible pipe, tube, hose, toys, electrical cable sheathing, e.g., Benvic, Darvic, Geon, Hostalit, Solvic, Vinoflex, Welvic.

(continued)

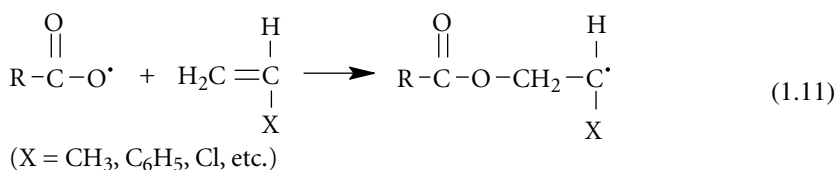
TABLE 1.1 (Continued)

	Monomer	Polymer	Comments
7.	Tetrafluoroethylene $\text{CF}_2=\text{CF}_2$	Polytetrafluoroethylene $\text{—}(\text{CF}_2=\text{CF}_2)\text{—}$	High Temperature resistance, chemically inert, excellent electrical insulator, very low coefficient of friction, expensive; moldings, films, coatings, used for non-stick surfaces, insulation, gaskets; e.g. Teflon, Fluon
8.	Methyl methacrylate $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array}$	Poly(methyl methacrylate) (PMMA) $\text{—}(\text{CH}_2-\text{C}\begin{array}{c} \text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array})\text{—}_n$	Transparent sheets and moldings; more expensive than PS; known as <i>organic</i> glass, used for aeroplane windows; e.g., Perspex, Plexiglass, Lucite, Diakon, Vedril.
9.	Isobutylene $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{CH}_3 \end{array}$	Polyisobutylene (PIB) $\text{—}(\text{CH}_2-\text{C}\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array})\text{—}_n$	Lubricating oils, sealants, copolymerized with 0.5–2.5 mol% isoprene to produce Butyl rubber for tire inner tubes and inner liners of tubeless tires.
10.	Isoprene $\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	<i>cis</i> -1,4-Polyisoprene $\text{—}(\text{CH}_2-\text{C}\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}=\text{CH}_2 \end{array})\text{—}_n$	Tires, mechanical goods, footwear, sealants, caulking compounds, e.g., Coral, Natsyn, Clariflex I.
11.	Butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	<i>cis</i> -1,4-Polybutadiene $\text{—}(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)\text{—}_n$	Tires and tire products, e.g., <i>Cis</i> -4, Ameripol-CB, Diene.

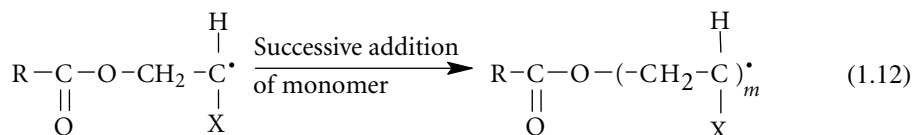
however, assumed to be the insertion of the first monomer molecule into a transition metal–carbon bond.) A free radical is a reactive substance having an unpaired electron and is usually formed by the decomposition of a relatively unstable material called an *initiator*. Benzoyl peroxide is a common free-radical initiator and can produce free radicals by thermal decomposition as



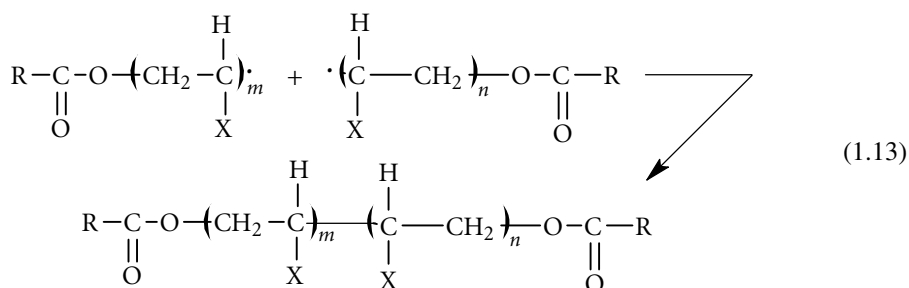
Free radicals are, in general, very active because of the presence of unpaired electrons (denoted by dot). A free-radical species can thus react to open the double bond of a vinyl monomer and add to one side of the broken bond, with the reactive center (unpaired electron) being transferred to the other side of the broken bond:



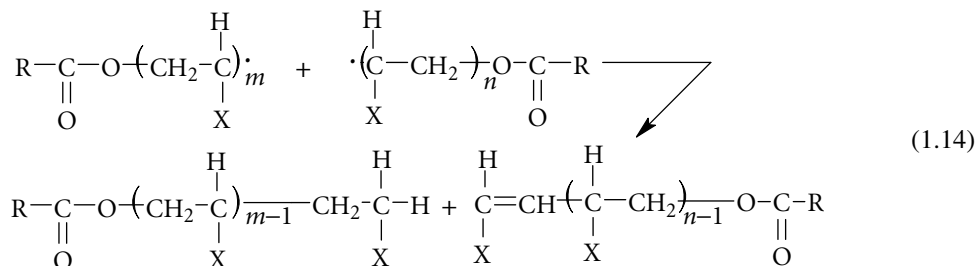
The new species, which is also a free radical, is able to attack a second monomer molecule in a similar way, transferring its reactive center to the attacked molecule. The process is repeated, and the chain continues to grow as a large number of monomer molecules are successively added to propagate the reactive center:



This process of propagation continues until another process intervenes and destroys the reactive center, resulting in the termination of the polymer growth. There may be several termination reactions depending on the type of the reactive center and the reaction conditions. For example, two growing radicals may combine to annihilate each other's growth activity and form an inactive polymer molecule; this is called termination by combination or coupling:



A second termination mechanism is disproportionation, shown by the following equation:



In chain polymerization initiated by free radicals, as in the previous example, the reactive center, located at the growing end of the molecule, is a free radical. Similarly, in chain polymerizations initiated by ionic systems, the reactive center is ionic, i.e., a carbonium ion (in cationic initiation) or a carbanion (in anionic initiation). Regardless of the chain initiation mechanism—free radical, cationic, or anionic—once a reactive center is produced it adds many more molecules in a chain reaction and grows quite large extremely rapidly, usually within a few seconds or less. (However, the relative slowness of the initiation stage causes the overall rate of reaction to be slow and the conversion of all monomers to polymers in most polymerizations requires at least 30 min, sometimes hours.) Evidently, at any time during a chain polymerization process the reaction mixture will consist only of unreacted monomers, high polymers and unreacted initiator species, but no intermediate sized molecules. The chain polymerization will thus show the presence of high-molecular-weight polymer molecules at all extents of conversion (see Figure 1.4). In certain ionic chain polymerizations, which feature a fast initiation process coupled with the absence of reactions that terminate the propagating reactive centers, molecular weight increases linearly with conversion. This is known as “living” ionic chain polymerization.

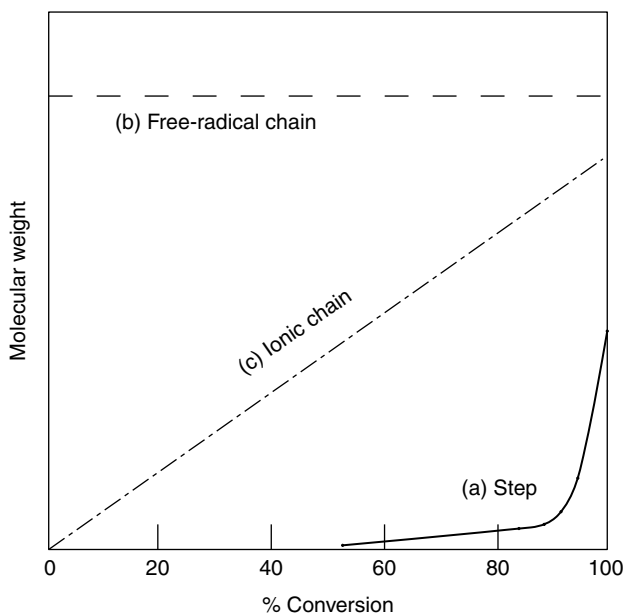


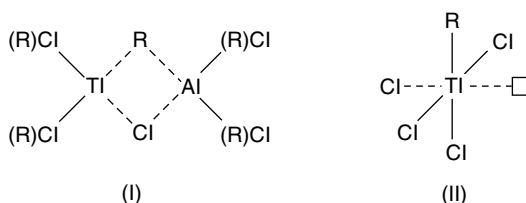
FIGURE 1.4 Variation of molecular weight with conversion in (a) step polymerization, (b) free-radical polymerization, and (c) ionic chain polymerization.

1.3.2 Coordination Addition Polymerization

Many polymers are now manufactured on a commercial scale using Ziegler–Natta catalysts, an outstanding example being polypropylene of high molecular weight which cannot be made by commercial processes of free-radical or ionic chain polymerization. Perhaps the best known Ziegler–Natta systems are those derived from TiCl_4 or TiCl_3 and an aluminum alkyl. The catalyst systems appear to function by formation of a coordination complex between the catalyst, growing chain, and incoming monomer. Hence the process is referred to as coordination addition polymerization and the catalysts as coordination catalysts. Polymers with stereoregular structures (see later) can be produced with these catalysts.

The efficiency or activity of the early Ziegler–Natta catalyst systems was low. The term activity usually refers to the rate of polymerization, expressed in terms of kilograms of polymer formed per gram of catalyst. Thus a low activity meant that large amounts of catalyst were needed to obtain reasonably high yields of polymer, and the spent catalyst had then to be removed from the product to avoid contamination. This problem effectively disappeared with the advent of subsequent generations of catalysts leading to large increases in activity without loss of stereospecificity. This was achieved by increasing the effective surface area of the active component by more than two orders of magnitude through impregnation of the catalyst on a solid support such as MgCl_2 or MgO . For example, in contrast to a typical $\text{TiCl}_3\text{--AlR}_3$ catalyst which yields about 50–200 g of polyethylene per gram of catalyst per hour per atmosphere of ethylene, as much as 200,000 g of polyethylene and over 40,000 g of polypropylene per gram titanium per hour may be produced using a MgCl_2 -supported catalyst, thus obviating the need to remove the spent catalyst (a costly step) from the product. Such catalyst systems are often referred to as high-mileage catalysts. Stereospecificity of the catalyst is kept high (>90%–98% isotactic dyads) by adding electron-donor additives such as ethyl benzoate.

The catalyst complex of the $\text{TiCl}_3/\text{AlR}_3$ system essentially acts as a template for the successive orientation and isotactic placement of the incoming monomer units. Though a number of structures have been proposed for the active species, they fall into either of two general categories: monometallic and bimetallic, depending on the number of metal centers. The two types can be illustrated by the structures (I) and (II) for the active species from titanium chloride (TiCl_4 or TiCl_3) and alkylaluminum (AlR_3 or AlR_2Cl).



Structure (I), representing a bimetallic species, is the coordination complex that arises from the interaction of the original catalyst components (titanium and aluminum compounds) with exchange of R and Cl groups. The placing of R and Cl groups in parentheses signifies that the exact specification of the ligands on Ti and Al cannot be made. Structure (II), representing a typical monometallic species, constitutes an active titanium site at the surface of a TiCl_3 crystal. Besides the four chloride ligands that the central Ti atom shares with its neighboring Ti atoms, it has an alkyl ligand (received through exchange reactions with alkyl aluminum) and a vacant orbital (\square).

The truly active bimetallic catalysts are complexes that have an electron-deficient bond, e.g., $\text{Ti}\cdots\text{C}\cdots\text{Al}$ in (I). Chain propagation by the bimetallic mechanism [7] occurs at two metal centers of the bridge complex as shown in Figure 1.5. With the chain growth taking place always from the metal end, the incoming monomer is oriented, for steric reasons, with the $=\text{CH}_2$ group pointing into the lattice and the CH_3 group to one side, with the result that the process leads to the formation of an isotactic polymer.

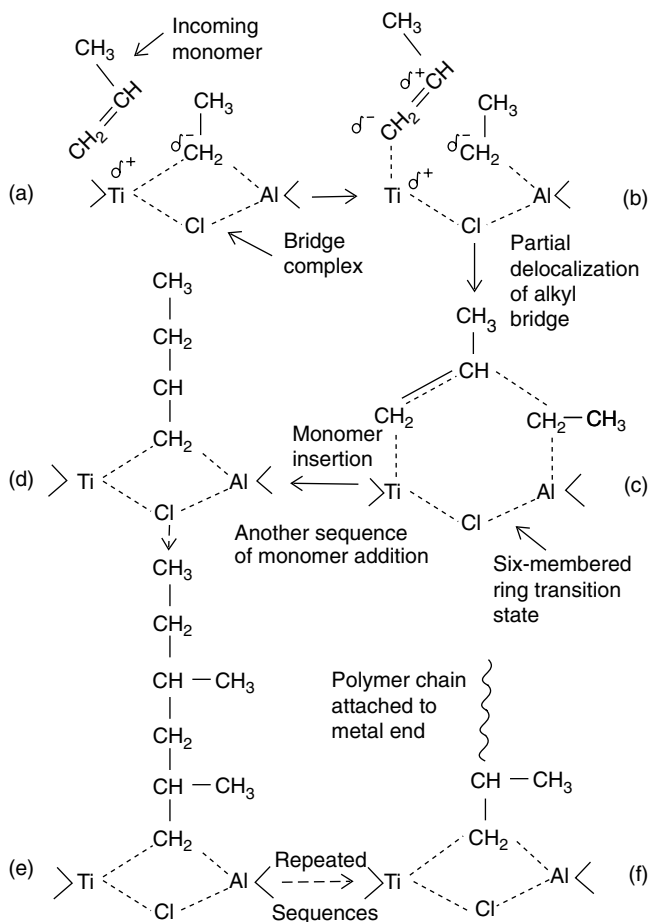


FIGURE 1.5 Bimetallic mechanism for stereospecific polymerization. (Adapted from Patat, F. and Sinn, H. 1958. *Angew. Chem.*, 70, 496.)

While a limited amount of experimental evidence does lend support to the bimetallic concept, majority opinion, however, favors the second and simpler alternative, the monometallic mechanism (described next).

It is generally accepted that the d-orbital in the transition element are the main source of catalytic activity and that it is the Ti-alkyl bond that acts as the polymerization center where chain growth occurs. For $\alpha\text{-TiCl}_3$ catalyst the active center [8] is formed by the interaction of aluminum alkyl with an octahedral vacancy around Ti, as shown in Figure 1.6. To elaborate, the five-coordinated Ti^{3+} on the surface has a vacant d-orbital, represented by \square , which facilitates chemisorption of the aluminum alkyl and this is followed by alkylation of the Ti^{3+} ion by an exchange mechanism to form the active center $\text{TiRCl}_4\text{-}\square$. The vacant site at the active center can accommodate the incoming monomer unit, which forms a π -complex with the titanium at the vacant d-orbital and is then inserted into the Ti-alkyl bond. The sequence of steps is shown in Figure 1.7 using propylene as the monomer.

After the monomer is inserted into the Ti-alkyl bond, the polymer chain migrates back to its initial position, while the vacant site migrates to its original position to accept another monomer molecule. This migration is necessary, as otherwise an alternating position would be offered to the monomer leading to the formation of a syndiotactic polymer instead of an isotactic polymer.

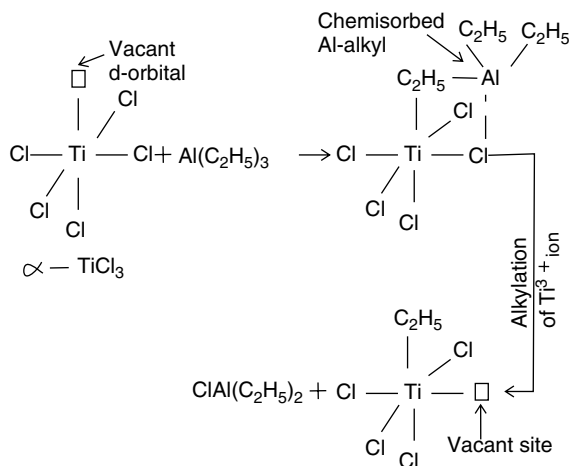


FIGURE 1.6 Interaction of aluminum alkyl with an octahedral vacancy around Ti in the first stage of monometallic mechanism. (After Cossee, P. 1967. *The Stereochemistry of Macromolecules*, A. D. Ketley, ed., Vol. 6. Marcel Dekker, New York.)

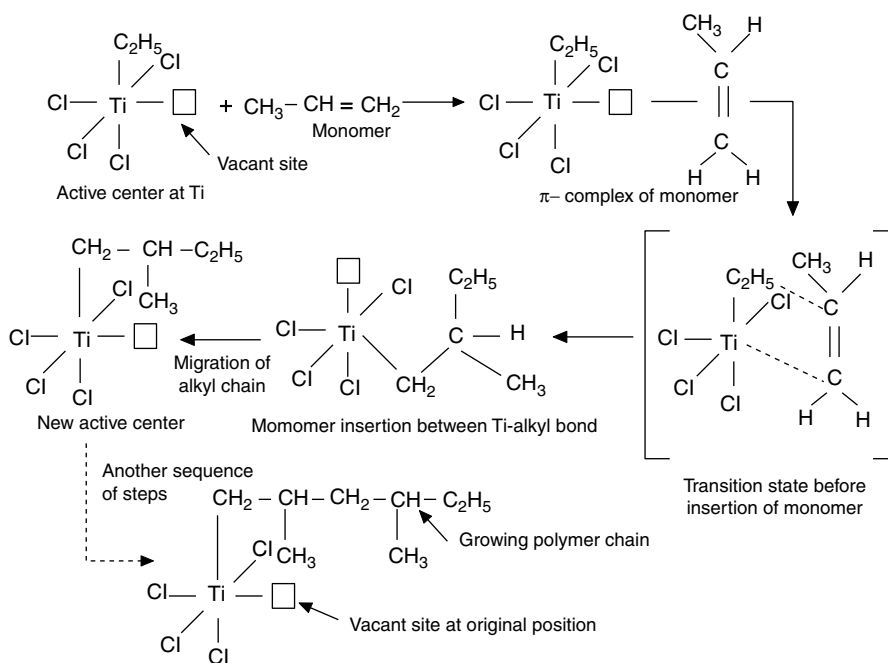
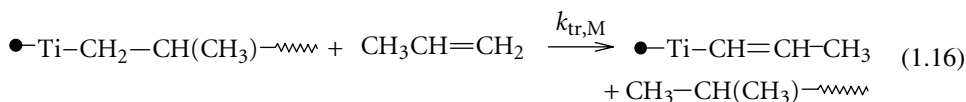
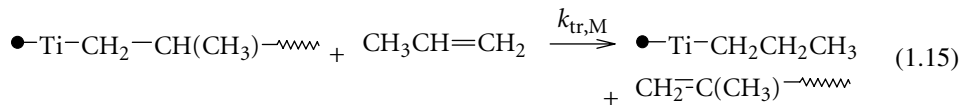


FIGURE 1.7 Monometallic mechanism for stereospecific polymerization. (After Cossee, P. 1967. *The Stereochemistry of Macromolecules*, A. D. Ketley, ed., Vol. 6. Marcel Dekker, New York.)

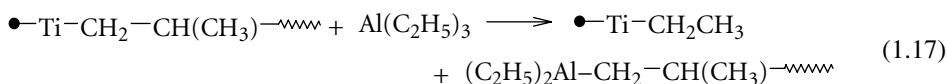
The termination of a polymer chain growing at an active center may occur by various reactions, as shown below with propylene as the example.

1. *Chain Transfer to Monomer:*

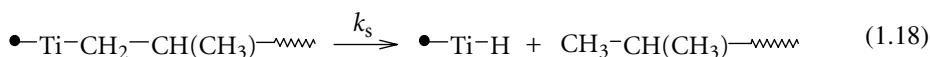


where $\bullet\text{-Ti}$ represents the transition metal active center on the catalyst site at which chain propagation takes place. Note that it is the methylene carbon atom from the monomer that is bonded to the transition metal atom (cf. [Figure 1.5](#)).

2. *Chain transfer to the Group I–III metal alkyl:*



3. *Spontaneous intramolecular-hydride transfer:*



4. *Chain transfer to an active hydrogen compound such as molecular hydrogen (external agent):*



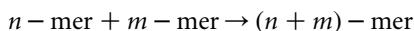
The above reactions terminating the growth of polymer chains are indeed chain transfer reactions since in each case a new propagating chain is initiated. The relative extents of these reactions depend on various factors such as the monomer, the initiator components, temperature, concentrations, and other reaction conditions. Under normal conditions of polymerization, intramolecular hydride transfer is negligible and termination of propagating chains occurs mostly by chain transfer processes. Being a highly effective chain transfer agent, molecular hydrogen is often used for polymer molecular weight control.

1.3.3 Step Polymerization

Step polymerization occurs by stepwise reaction between functional groups of reactants. The reaction leads successively from monomer to dimer, trimer, tetramer, pentamer, and so on, until finally a polymer molecule with large DP is formed. Note, however, that reactions occur at random between the intermediates (e.g., dimers, trimers, etc.) and the monomer as well as among the intermediates themselves. In other words, reactions of both types, namely,

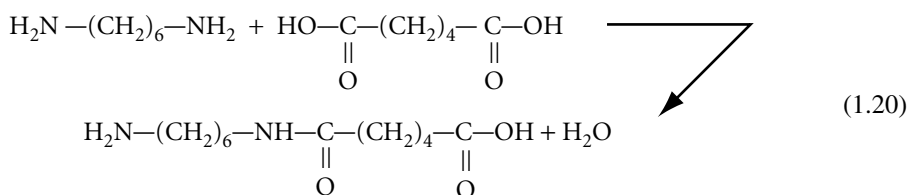


and

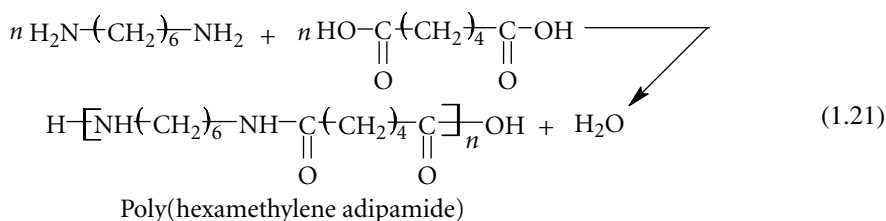


occur equally. Thus, at any stage the product consists of molecules of varying sizes, giving a range of molecular weights. The average molecular weight builds up slowly in the step polymerization process, and a high-molecular-weight product is formed only after a sufficiently long reaction time when the conversion is more than 98% (see Figure 1.4a).

Since most (though not all) of the step polymerization processes involve poly-condensation (repeated condensation) reactions, the terms step polymerization and condensation polymerization are often used synonymously. Consider, for example, the synthesis of a polyamide, i.e., a polymer with amide ($-\text{CONH}-$) as the characteristic linkage. If we start with, say, hexamethylenediamine and adipic acid as reactants, the first step in the formation of the polymer (nylon) is the following reaction producing a monoamide:



The reaction continues step-by-step to give the polyamide nylon-6,6. The overall reaction may thus be represented as



We see that the composition of the repeating unit (enclosed in square brackets) equals that of two monomer molecules minus two molecules of water. Thus a condensation polymer may be defined as one whose synthesis involves elimination of small molecules or whose repeating unit lacks certain atoms present in the monomer(s).

With the development of polymer science and the synthesis of new polymers, the previous definition of condensation polymer is inadequate. For example, in polyurethanes (Table 1.2), which are classified as condensation polymers, the repeating unit has the same net composition as the two monomers (i.e., a diol and a diisocyanate), which react without eliminating any small molecule. To overcome such problems, chemists have introduced a definition which describes condensation polymers as consisting of structural units joined by internal functional groups such as

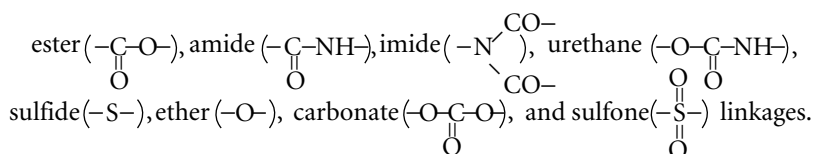
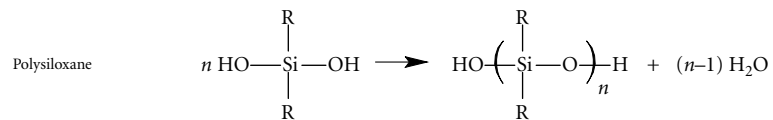
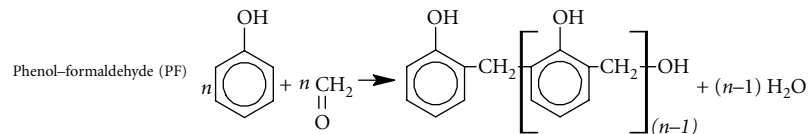


TABLE 1.2 Typical Condensation Polymers

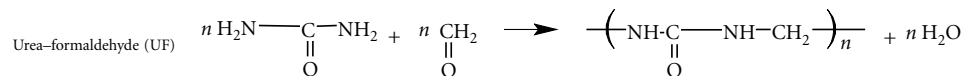
	Polymerization Reaction ^a	Comments
Polyamide (PA)	$n \text{ H}_2\text{N}-\text{R}-\text{NH}_2 + n \text{ HO}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}'-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH} \longrightarrow \text{H}-\left(\text{NH}-\text{R}-\underset{\text{O}}{\underset{\parallel}{\text{NHC}}}-\text{R}'-\underset{\text{O}}{\underset{\parallel}{\text{C}}}\right)_n\text{OH} + (2n-1) \text{ H}_2\text{O}$ $n \text{ H}_2\text{N}-\text{R}-\text{NH}_2 + n \text{ Cl}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}'-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{Cl} \longrightarrow \text{H}-\left(\text{NH}-\text{R}-\underset{\text{O}}{\underset{\parallel}{\text{NHC}}}-\text{R}'-\underset{\text{O}}{\underset{\parallel}{\text{C}}}\right)_n\text{Cl} + (2n-1) \text{ HCl}$ $n \text{ H}_2\text{N}-\text{R}-\underset{\text{O}}{\underset{\parallel}{\text{COH}}} \longrightarrow \text{H}-\left(\text{NH}-\text{R}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}\right)_n\text{OH} + (n-1) \text{ H}_2\text{O}$	Moldings, fibers, tirecord; poly(hexamethylene adipamide) (Nylon 6,6) e.g., Ultramid A; polycaprolactam (nylon-6), e.g., Ultramid B, Akulon, Perlenka, poly(hexamethylene sebacamide) (Nylon-6,10), e.g., Ultramid S, Zytel.
Polyester	$n \text{ HO}-\text{R}-\text{OH} + n \text{ HO}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}'-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH} \longrightarrow \text{HO}-\left(\text{R}-\underset{\text{O}}{\underset{\parallel}{\text{OC}}}-\text{R}'-\underset{\text{O}}{\underset{\parallel}{\text{CO}}}\right)_n\text{H} + (2n-1) \text{ H}_2\text{O}$ $n \text{ HO}-\text{R}-\text{OH} + n \text{ R}''\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}'-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OR}'' \longrightarrow \text{HO}-\left(\text{R}-\underset{\text{O}}{\underset{\parallel}{\text{OC}}}-\text{R}'-\underset{\text{O}}{\underset{\parallel}{\text{CO}}}\right)_n\text{R}'' + (2n-1) \text{ R}''\text{OH}$ $n \text{ HO}-\text{R}-\underset{\text{O}}{\underset{\parallel}{\text{COH}}} \longrightarrow \text{HO}-\left(\text{R}-\underset{\text{O}}{\underset{\parallel}{\text{CO}}}\right)_n\text{H} + (n-1) \text{ H}_2\text{O}$	Textile fibers, film, bottles; poly(ethylene terephthalate) (PET) e.g., Terylene, Dacron, Melinex, Mylar.
Polyurethane (PU)	$n \text{ HO}-\text{R}-\text{OH} + n \text{ OC}:\text{N}-\text{R}'-\text{NCO} \longrightarrow \text{H}-\left(\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{R-OC}}}-\underset{\text{O}}{\underset{\parallel}{\text{NH}}}-\text{R}'-\underset{\text{O}}{\underset{\parallel}{\text{NHC}}}\right)_{(n-1)}\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{R-OC}}}-\underset{\text{O}}{\underset{\parallel}{\text{NH}}}-\text{R}'-\text{NCO}$	Rubbers, foams, coatings; e.g., Vulkollan, Adiprene C, Chemigum SL, Desmophen A, Moltopren.
Polysulphide	$n \text{ Cl}-\text{R}-\text{Cl} + n \text{ Na}_2\text{S}_x \longrightarrow \left(\text{R}-\text{S}_x\right)_n + 2n \text{ NaCl}$	Adhesives, sealants, binders, hose, e.g., Thiokol.



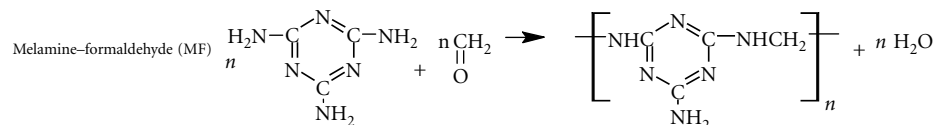
Elastomers, sealants, fluids, e.g., Silastic, Silastomer, Silopren.



Plywood adhesives, glass-fiber insulation, molding compound, e.g., Hitanol, Sirfen, Trolitan.



Particle-board binder resin, paper and textile treatment, molding compounds, coatings, e.g., Beetle, Resolite, Cibanoid.

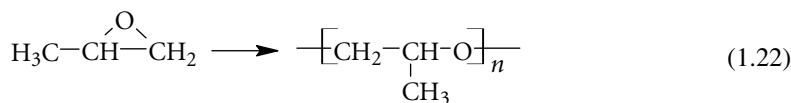


Dinnerware, table tops, coatings, e.g., Formica, Melalam, Cymel.

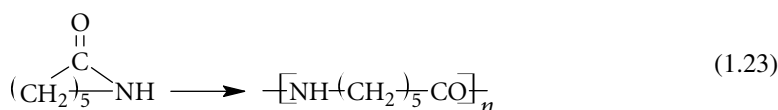
^a R, R', R'' represent aliphatic or aromatic ring. The repeating unit of the polymer chain is enclosed in parentheses.

A polymer satisfying either or both of the above definitions is classified as a condensation polymer. Phenol–formaldehyde, for example, satisfies the first definition but not the second. Some condensation polymers along with their repeating units and condensation reactions by which they can be synthesized are shown in Table 1.2. Some high-performance polymers prepared by polycondensation are listed in Table 1.3.

The ring-opening polymerizations of cyclic monomers, such as propylene oxide,



or ϵ -caprolactam



proceed either by chain or step mechanisms, depending on the particular monomer, reaction conditions, and initiator employed. However, the polymers produced in Equation 1.22 and Equation 1.23 will be structurally classified as condensation polymers, since they contain functional groups (e.g., ether, amide) in the polymer chain. Such polymerizations thus point out very clearly that one must distinguish between the classification based on polymerization mechanism and that based on polymer structure. The two classifications cannot always be used interchangeably. Both structure and mechanism are usually needed in order to clearly classify a polymer.

1.3.4 Supramolecular Polymerization

Supramolecular polymers are a relatively new class of polymers in which monomeric repeating units are held together with directional and reversible (noncovalent) secondary interactions, unlike conventional macromolecular species in which repetition of monomeric units is mainly governed by covalent bonding. A schematic comparison of a covalent polymer and a supramolecular polymer is shown in Figure 1.8.

The directionality and strength of the supramolecular bonding, such as hydrogen bonding, metal coordination, and π – π interactions, are important features resulting in polymer properties in dilute and concentrated solutions, as well as in the bulk. It should be noted that supramolecular interactions are not new to polymer science, where hydrogen bonding and other weak reversible interactions are important in determining polymer properties and architectures. However, for linear supramolecular polymers to form, it is a prerequisite to have strong and highly directional interactions as a reversible alternative for the covalent bond. Hydrogen bonds between neutral organic molecules, though they hold a prominent place in supramolecular chemistry because of their directionality and versatility, are not among the strongest noncovalent interactions. Hence, either multiple hydrogen bonds with cooperativity must be used or hydrogen bonds should be supported by additional forces like excluded volume interactions [9]. Though the concept has been known for years, it was not known how to incorporate such sufficiently strong but still reversible interactions. However, in the past decade following the development of strong hydrogen-bonding dimers, several research groups have applied these dimers for the formation of hydrogen-bonded supramolecular polymers. Thus the finding by Sijbesma et al. [10] that derivatives of 2-ureido-4[1H]-pyrimidinone (UPy, **1** in Figure 1.9) are easy to synthesize and they dimerize strongly (dimerization constant $> 10^6 \text{ M}^{-1}$ in CHCl_3) by self-complementary quadrupole (array of four) hydrogen bonding (**2** in Figure 1.9) prompted them to use this functionality as the associating end group in reversible self-assembling polymer systems.

TABLE 1.3 Some High-Performance Condensation Polymers

Polymer Type and Polycondensation Reaction	Comments
<p>Polycarbonate (PC)</p> $n \text{ HO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{OH} + n \text{ Cl}-\text{C}(=\text{O})-\text{Cl} \longrightarrow \left[\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{C}(=\text{O}) \right]_n + (2n-1) \text{ HCl}$	<p>Moldings and sheets; transparent, tough and physiologically inert: used for safety glasses, lenses, screens and glazings, electrical and electronics, appliances, compact discs, e.g. Merlon, Baylon, Jupilon.</p>
<p>Polyether sulfone (PES)</p> $n \text{ KO}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-\text{Cl} \longrightarrow \left[\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_n + (n-1) \text{ KCl}$	<p>Moldings, coatings, membranes; rigid, transparent, self-extinguishing, resistant to heat deformation: used for electrical components, molded circuit boards, appliances operating at high temperatures, e.g., Victrex PES.</p>
<p>Polyetheretherketone (PEEK)</p> $n \text{ KO}-\text{C}_6\text{H}_4-\text{OK} + n \text{ F}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{F} \longrightarrow \left[\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{C}_6\text{H}_4 \right]_n + (2n-1) \text{ KF}$	<p>Moldings, composites, bearings, coatings; very high continuous use temperature (260°C): used in coatings and insulation for high performance wiring, composite prepregs with carbon fibers, e.g., Victrex PEEK.</p>
<p>Poly(phenylene sulphide) (PPS)</p> $n \text{ Cl}-\text{C}_6\text{H}_4-\text{Cl} + n \text{ Na}_2\text{S} \longrightarrow \left[\text{C}_6\text{H}_4-\text{S} \right]_n + (2n-1) \text{ NaCl}$	<p>Moldings, composites, coatings; outstanding in heat resistance, flame resistance, chemical resistance and electrical insulation resistance; used for electrical components, mechanical parts, e.g., Ryton, Tedur, Fortron.</p>

(continued)

TABLE 1.3 (Continued)

Polymer Type and Polycondensation Reaction	Comments
<p>Poly(<i>p</i>-phenylene terephthalamide)</p> $n \text{ Cl}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Cl} + n \text{ H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2 \longrightarrow \left[\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{NH}-\text{C}_6\text{H}_4-\text{NH} \right]_n + (2n-1) \text{ NaCl}$	<p>High modulus fibers; as strong as steel but have one-fifth of weight, ideally suited as tire cord materials and for ballistic vests, e.g., Kevlar, Twaron.</p>
<p>Polyimide</p> $n \text{ O}=\text{C}_6\text{H}_2(\text{C}=\text{O})_2\text{O} + n \text{ H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2 \longrightarrow \left[\text{N}(\text{C}_6\text{H}_4)\text{N}(\text{C}_6\text{H}_2(\text{C}=\text{O})_2)_2 \right]_n + (2n-1) \text{ H}_2\text{O}$	<p>Films, coatings, adhesives, laminates; outstanding in heat resistance, flame resistance, abrasion resistance, electrical insulation resistance, resistance to oxidative degradation, high energy radiation and most chemicals (except strong bases): used in specialist applications, e.g., Kapton, Vespel.</p>

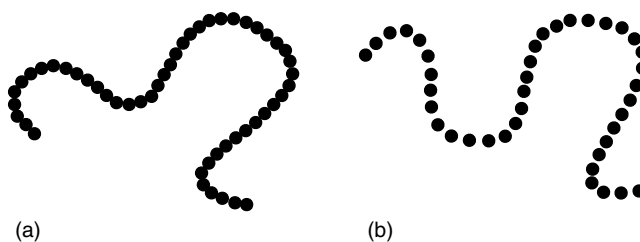


FIGURE 1.8 Schematic representation of (a) a covalent polymer and (b) a supramolecular polymer. (After Brunsveld, L., Folmer, B. J. B., Meijer, E. W., and Sijbesma, R. P. 2001. *Chem. Rev.*, 101, 4071. With permission.)

A difunctional UPy compound, **4** in Figure 1.10, possessing two UPy units can be easily made in a one step procedure, from commercially available compounds, methylisocyanate ($R=CH_3$) and hexyldiisocyanate ($R=C_6H_{12}$). The compound forms very stable and long polymer chains (**5** in Figure 1.10) in solution as well as in the bulk [9,11]. Dissolving a small amount of the compound in chloroform gives solutions with high viscosities, while calculations show that polymers with molecular weights of the order of 10^6 can be formed. Deliberate addition of small amounts of monofunctional compounds (**1** in Figure 1.9) results in a sharp drop in viscosity, proving that linkages between the building blocks are reversible and unidirectional and that the monofunctional compounds act as chain stoppers. For the same reason, the supramolecular polymers show polymer-like viscoelastic behavior in bulk and solution, whereas at elevated temperatures they exhibit liquid-like properties [9].

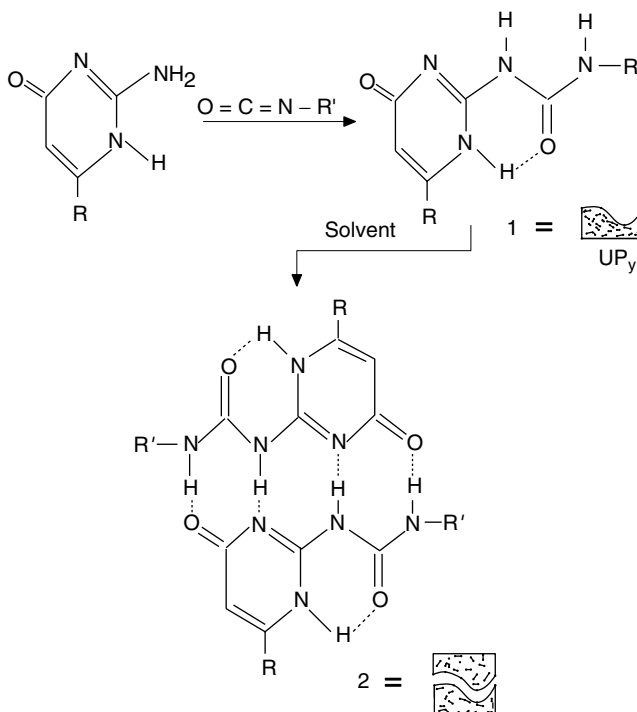


FIGURE 1.9 Synthesis of a monofunctional 2-ureido-4[1H]-pyrimidinone (UPy) (**1**) and dimerization of **1** in solution forming a quadrupole hydrogen-bonded unit. (After Sijbesma, R. P., Beijer, F. H., Brunsveld, L., Folmer, B. J. B., Hirschberg, J. H. K., Lange, R. F. M., Lowe, J. K. L., and Meijer, E. W. 1997. *Science*, 278, 1601. With permission.)

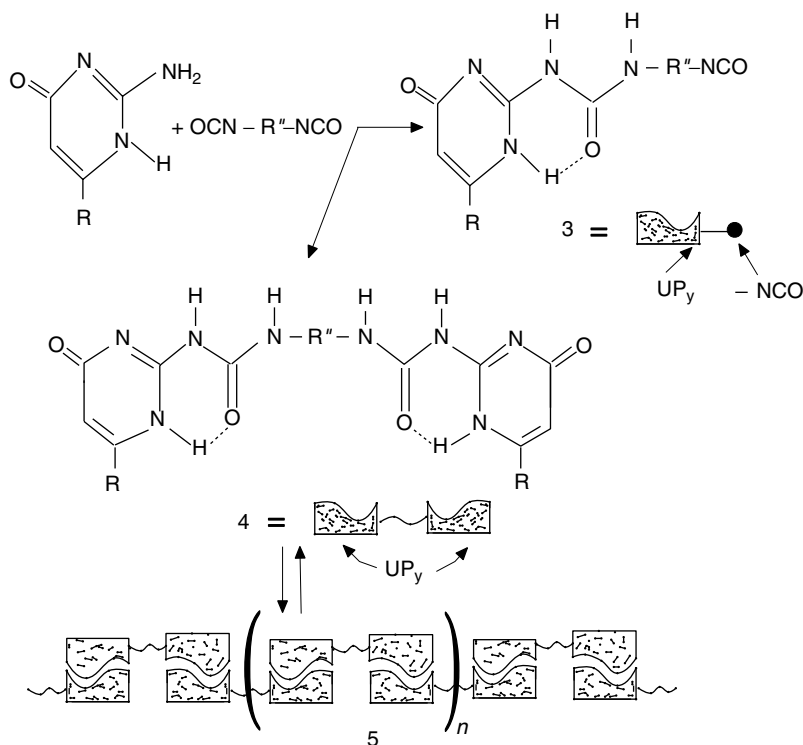


FIGURE 1.10 Preparation of (a) UPy possessing an isocyanate functional group (3) and (b) a difunctional UPy compound (4) which forms a supramolecular polymer (5) by hydrogen bonding (cf. Figure 1.9). (After Brunsveld, L., Folmer, B. J. B., Meijer, E. W., and Sijbesma, R. P. 2001. *Chem. Rev.*, 101, 4071 and Folmer, B. J. B., Sijbesma, R. P., Versteegen, R. M., van der Rijt, J. A. J., and Meijer, E. W. 2000. *Adv. Mater.*, 12, 12, 874. With permission.)

The quadrupole hydrogen-bonded unit can be employed in the chain extension of telechelic oligomers such as polysiloxanes, polyethers, polyesters, and polycarbonates [11]. Thus the electrophilic isocyanate group (-NCO) of “synthon” (3 in Figure 1.10) can be reacted with common nucleophilic end groups (-OH or -NH_2) of telechelic oligomers, resulting in supramolecular polymers by chain extension (Figure 1.11). Thus the material properties of telechelic polymers have been shown to improve dramatically upon functionalization with synthon, and materials have been obtained that combine many of the mechanical properties of conventional macromolecules with the low melt viscosity of oligomers [9]. In contrast to conventional high-molecular-weight polymers, supramolecular (reversible) polymers with a high “virtual” molecular weight show excellent processability due to the strong temperature dependency of the melt viscosity [11]. Moreover, hybrids between blocks of covalent macromolecules and supramolecular polymers can be easily made.

1.3.5 Copolymerization

All the addition polymers we have considered so far (Table 1.1) contain only one type of repeating unit or mer in the chain. Polymers can also be synthesized by the aforesaid processes with more than one type of mer in the chain. Such polymers are called *copolymers*. They are produced by polymerizing a mixture of monomers (copolymerization) [12] or by special methods. Copolymers can be of different types, depending on the monomers used and the specific method of synthesis. The copolymer with a relatively random distribution of the different mers in its structure is referred to as a random copolymer. Representing, say, two different mers by A and B, a random copolymer can be depicted as

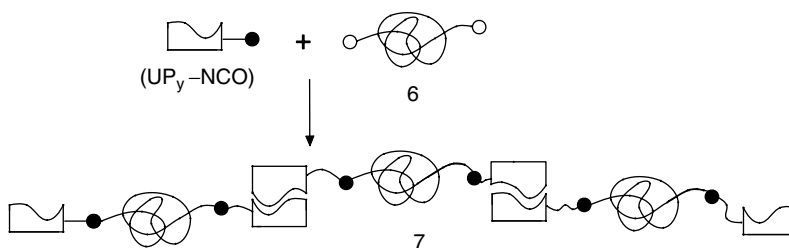


FIGURE 1.11 Schematic representation of the formation of supramolecular polymer (7) by chain extension of reactive telechelic oligomer with UPy. (After Folmer, B. J. B., Sijbesma, R. P., Versteegen, R. M., van der Rijt, J. A. J., and Meijer, E. W. 2000. *Adv. Mater.*, 12, 12, 874. With permission.)

ABBABBBBAABBAABAAABBA

There other copolymer structures [13] are known: alternating, block, and graft copolymer structures (Figure 1.12). In the alternating copolymer the two mers alternate in a regular fashion along the polymer chain:

ABABABABABABABABABAB

A block copolymer is a linear copolymer with one or more long uninterrupted sequences of each mer in the chain:

AAAAAAAAAABBBBBBBBBB

A graft copolymer, on the other hand, is a branched copolymer with a backbone of one type of mer to which are attached one or more side chains of another mer.

AAAAAAAAAAAAAAAAAAAA

B
B
B
B
B

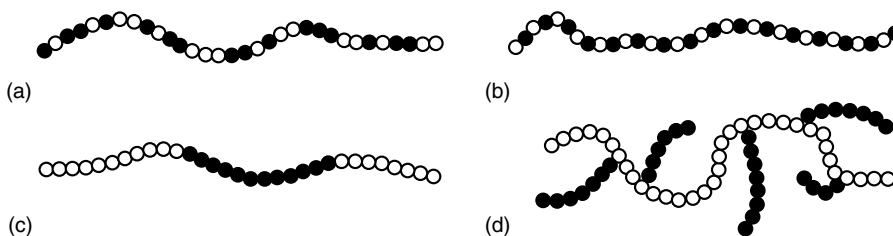


FIGURE 1.12 Copolymer arrangements. (a) Two different types of mers (denoted by open and filled circles) are randomly placed. (b) The mers are alternately arranged. (c) A block copolymer. (d) A graft copolymer.

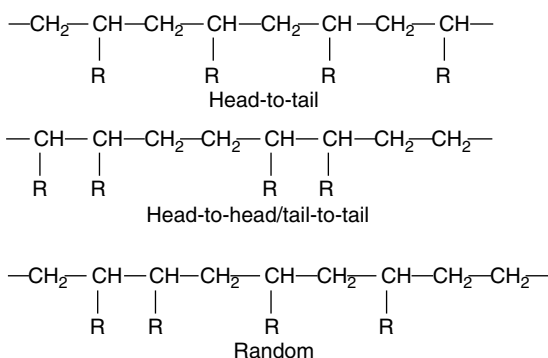
Copolymerization, which may be compared to alloying in metallurgy, is very useful for synthesizing polymers with the required combination of properties. For example, polystyrene is brittle and polybutadiene is flexible; therefore copolymers of styrene and butadiene should be more flexible than polystyrene but tougher than polybutadiene. The general-purpose rubber GRS (or SBR), the first practical synthetic rubber, is a copolymer of styrene and butadiene.

1.4 Configurations of Polymer Molecules

The long threadlike shape of polymer molecules induces generally a random arrangement leading to inter- and intramolecular entanglement, somewhat like a bowl of cooked spaghetti. A typical molecule of polyethylene, for example, might be represented by a cylindrical chain with a length of 50,000 Å and a diameter of less than 5 Å. This is similar to a rope that is 45 m long and 4.5 mm in diameter. A molecule such as this can easily get knotted and entangled with surrounding molecules. In the structure some parts of the molecular chains can be more ordered than others. The ordered regions are termed micelles or *crystallites*. These regions are embedded in the unordered or amorphous matrix.

It is quite logical that if we want a molecule to go into some kind of ordered, repetitive pattern, then its structure must also have a regularly repeating pattern. The degree of crystallinity of the polymer will thus increase with the linearity and steric regularity of the molecules and also with interchain attractive forces.

Linear polymers are found in nature, or they may be formed by polymerization of simple monomers. When monosubstituted ethylene monomers ($\text{CH}_2=\text{CHR}$) polymerize, the addition reaction may be head-to tail, head-to-head/tail-to-tail, or a random mixture of the two:



The head-to-tail configuration is preferred almost to the exclusion of the other two. An important reason for this is steric hindrance, which favors head-to-tail reaction, especially if R is bulky.

Another aspect of stereoregularity is tacticity. Figure 1.13 show a polymer chain in which all of the chain carbons are in the same plane. Three configurations can be obtained: A polymer molecule is isotactic if all the substituted groups lie on the same side of the main chain. In a syndiotactic polymer molecule the substituted groups regularly alternate from one side to the other. The molecule is *atactic* if the positioning of substituted groups is random.

The relative arrangement of groups and atoms in successive monomer units in a polymer chain not only affects the crystallinity but also induces completely different properties in polymers. One example of this effect is found in polypropylene stereoisomers. (The three stereoisomers of polypropylene can be obtained by replacing R by CH_3 in Figure 1.13.) The structural difference results in profound variations in the properties of polypropylene isomers. As is evident from Table 1.4, the three polypropylene isomers appear to be three altogether different materials.

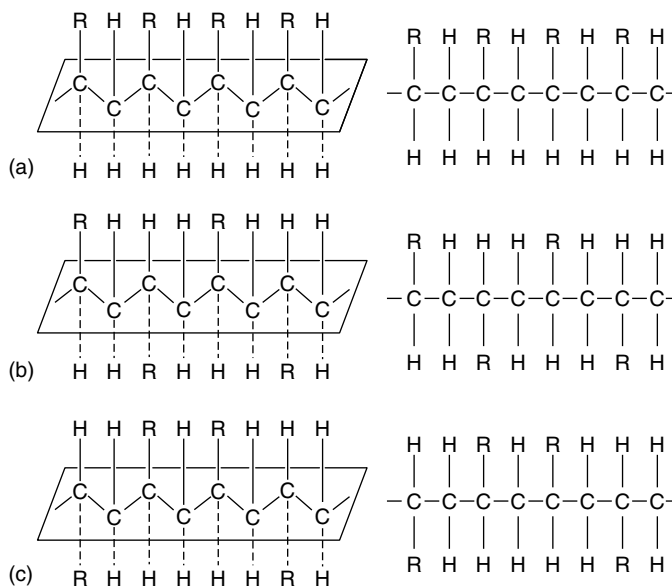


FIGURE 1.13 Diagrams of (a) isotactic, (b) syndiotactic, and (c) atactic configuration in a vinyl polymer. The corresponding Fischer projections are shown on the right.

1.5 Conformations of a Polymer Molecule

Just as a rope can be stretched, folded back on itself, curled up into a ball, entangled, knotted, and so forth, a polymer molecule can take on many conformations. Consider a molecule as a chain of N links, each link of length l_0 and attached to the preceding link by a rotating joint.

For a free rotating polymer chain the average conformation is characterized by the mean square distance $\langle r^2 \rangle$ between the ends of the chain and is given by

$$\langle r^2 \rangle = Nl_0^2 \quad (1.24)$$

If we assume that adjacent links in the chain form fixed angles θ with each other but rotate freely about that angle, then

$$\langle r^2 \rangle = \frac{1 - \cos \theta}{1 + \cos \theta} Nl_0^2 = 2Nl_0^2 \quad (1.25)$$

since bonds in a tetrahedral carbon unit are at 109.5° to each other.

Thus, for a polyethylene molecule comprising, say, 40,000 freely rotating $-\text{CH}_2-$ units ($l_0 = 1.54 \text{ \AA}$), the end-to-end distance would only be $\sqrt{2N} l_0$ or approximately 435 \AA . In contrast, if fully extended, the molecule will be in all-*trans* conformation with a linear zigzag structure (like corrugated sheets) shown in (III). (The dotted lines denote bonds and the wedges signify bonds above the plane of the page.)

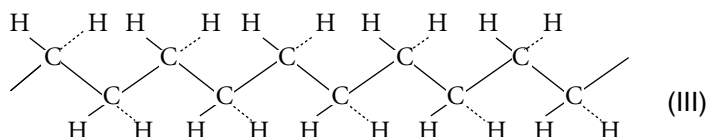


TABLE 1.4 Properties of Polypropylene Stereoisomers

Property	Stereoisomers		
	Isotactic	Syndiotactic	Atactic
Appearance	Hard solid	Hard solid	Soft rubbery
Melting temperature (°C)	175	131	< 100
Density (g/cc)	0.90–0.92	0.89–0.91	0.86–0.89
Tensile strength [psi (N/m ²)]	5,000 (3.4×10^7)	—	—
Solubility	Insoluble in most organic solvents	Soluble in ether and aliphatic hydrocarbon	Soluble in common organic solvents
Crystallinity (%)	< 70	—	—
Glass transition temperature (°C)	0 to –35	—	–11 to –35

The end-to-end distance of this fully extended polyethylene molecule will be $Nl_0 \sin(109.5^\circ/2)$, or approximately 50,000 Å, for a molecule comprising 40,000 $-\text{CH}_2-$ units, and the contour length is Nl_0 or 60,000 Å.

1.6 Polymer Crystallinity

X-ray scattering and electron microscopy have shown that the crystallites are made up of lamellae which, in turn, are built-up of folded polymer chains as explained below.

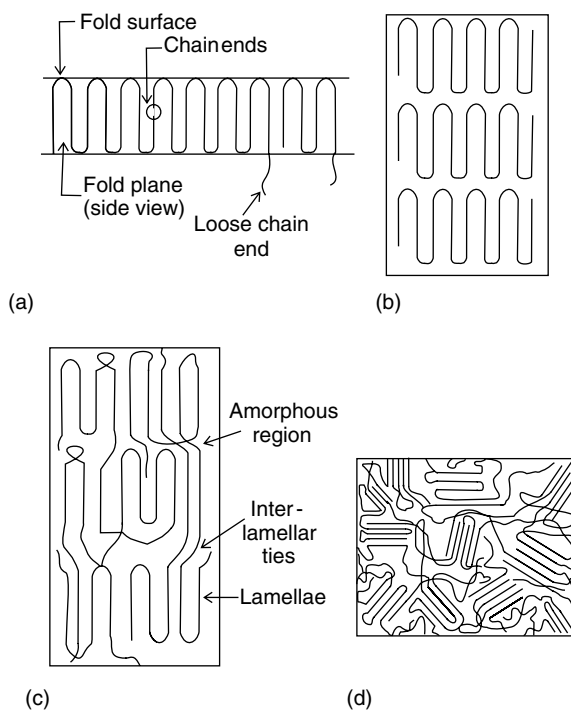


FIGURE 1.14 Schematic representation of (a) fold plane showing regular chain folding, (b) ideal stacking of lamellar crystals, (c) interlamellar amorphous model, and (d) fringed micelle model of randomly distributed crystallites.

Lamellae are thin, flat platelets on the order of 100–200 Å (0.01–0.02 μm) thick and several microns in lateral dimensions, while polymer molecules are generally on the order of 1,000–10,000 Å long. Since the polymer chain axis is perpendicular to the plane of the lamellae, as revealed by electron diffraction, the polymer molecules must therefore be folded back and forth within the crystal. This arrangement has been shown to be sterically possible. In polyethylene, for example, the molecules can fold in such a way that only about five chain carbon atoms are required for the fold, that is, for the chain to reverse its direction. Each molecule folds up and down in a regular fashion to establish a fold plane. As illustrated in Figure 1.14a, a single fold plane may contain many polymer chains. The height of the fold plane is known as the fold period. It corresponds to the thickness of the lamellae.

Figure 1.14b shows an idealized model of lamellae structure with ideal stacking of lamellar crystals. A more useful model, however, is that of stacks of lamellae interspersed with and connected by amorphous regions that consist of disordered chain segments of polymer molecules. Such a model, referred to as interlamellar amorphous model (Figure 1.14c), helps explain the ductility and strength of polymers as a direct consequence of the molecular links between the lamellae forming interlamellar ties. For semicrystalline polymers with amorphous regions to the tune of 20%–50%, it is often more advantageous to adopt a fringed micelle or fringed crystalline model (Figure 1.14d). It pictures polymers as two-phase systems in which the amorphous regions are interspersed between the randomly distributed crystallites.

1.6.1 Determinants of Polymer Crystallinity

The extent to which polymer molecules will crystallize depends on their structures and on the magnitudes of the secondary bonds forces among the polymer chains: the greater the structural regularity and symmetry of the polymer molecule and the stronger the secondary forces, the greater the tendency toward crystallization. We give a few examples:

1. Linear polyethylene has essentially the best structure for chain packing. Its molecular structure is very simple and perfectly regular, and the small methylene groups fit easily into a crystal lattice. Linear polyethylene (high density) therefore crystallizes easily and to a high degree (over 90%) even though its secondary forces are small. Branching impairs the regularity of the structure and makes chain packing difficult. Branched polyethylene (low density) is thus only partially (50%–60%) crystalline. Most of the differences in properties between low-density and high-density polyethylenes can be attributed to the higher crystallinity of the latter. Thus, linear polyethylenes have higher density than the branched material (density range of 0.95–0.97 versus 0.91–0.94 g/cm³), higher melting point (typically 135 versus 115°C), greater stiffness (modulus of 100,000 versus 20,000 psi), greater tensile strength, greater hardness, and less permeability to gases and vapors.
2. Substituents hanging off polymer chains lead to difficulties in packing and generally decrease the tendency toward crystallization. Moreover, crystallization does not take place easily when polymer molecules have a low degree of symmetry. Thus, polymers such as polystyrene, poly(methyl methacrylate), poly(vinyl acetate), etc., all of which have bulky side groups oriented at random with respect to the main carbon chain (in atactic polymers), show very poor crystallization tendencies and tend to have amorphous structures. However, crystallinity would result if the side groups could be arranged in a regular orientation. Indeed, this can be done by controlled polymerization with properly chosen catalysts.
3. Copolymerization reduces the structural symmetry of a polymer. Thus it is a very effective method of decreasing the crystallization tendency of a polymer.
4. Chain flexibility also affects the crystallizability of a polymer. Excessive flexibility in a polymer chain, as in natural rubber and polysiloxanes, gives rise to difficulty in chain packing, with the result that such polymers remain almost completely in the amorphous state. In the other extreme, excessive rigidity in polymers due to extensive cross-linking, as in thermosetting resins like phenol–formaldehyde and urea–formaldehyde, also results in an inability to crystallize.

5. The presence of polar groups—such as amide, carboxyl, hydroxyl, chlorine, fluorine, and nitrile—along the polymer chains greatly increases the intermolecular or secondary attraction forces, which is favorable for crystallization. However, high secondary forces alone may not give rise to high crystallinity unless the chain segments are aligned. Mechanical stretching of the polymer makes this alignment easier. For example, nylon-6,6 (a polyamide) has less than the expected degree of crystallinity in the unstretched condition and is used as a plastic. Highly crystalline strong fibers are produced by stretching (cold-drawing) the polyamide polymer 400%–500%. Mechanical stretching also makes it possible to develop a degree of order and crystallinity in several other thermoplastic resins that do not ordinarily crystallize. An unusual example of alignment and crystallization on stretching is rubber.
6. The degree of crystallinity of polymeric materials is reduced by adding plasticizers. Crystallization in many synthetic resins is not always desirable because it makes shaping more difficult and reduces transparency by closely packing neutralization of the intermolecular forces of attraction by coming between polymer molecules, thus enhancing flexibility and plasticity, are often added to the polymeric mass before shaping. The oldest example is celluloid, made by plasticizing nitrocellulose (ordinarily a crystalline material) with camphor. Cellophane (regenerated cellulose film produced by a *viscose* process) is plasticized with glycerine to prevent crystallization and loss of transparency. Polyvinyl chloride (PVC) is made flexible by adding plasticizers, such as dioctyl phthalate, for use as wire coating, upholstery, film and tubing. The unplasticized rigid PVC is used for the production of pipe, sheet, and molded parts. The disadvantage of plasticizers is that they reduce the tensile strength and chemical resistance of the material.

1.7 The Amorphous State

The amorphous state is the characteristic of all polymers at temperatures above their melting points (except under special circumstances where liquid crystals may form). If a molten polymer retains its amorphous nature on cooling to the solid state, the process is called vitrification. In the vitrified amorphous state, the polymer resembles a glass. It is characteristic of those polymers in the solid state that, for reasons of structure, exhibit no tendency toward crystallization. The amorphous solid state is characterized by glass transition (T_g), which is described in a later section. We consider below only the behavior of polymer melt.

When an amorphous polymer achieves a certain degree of rotational freedom, it can be deformed. If there is sufficient freedom, the molecules begin to move past one another and the polymer flows. The science of deformation and flow is called rheology. It is of fundamental importance in industrial applications since it is usually in the molten state that polymers are molded into useful objects.

To cause a polymer to deform or flow requires the application of a force. If a force is applied and then withdrawn quickly, the polymer molecules tend to revert to their previous undeformed configuration, a process called relaxation. In other words, the polymer melt exhibits a certain elastic quality. This elasticity comes about because the molecules were disturbed from what was a thermodynamically favorable arrangement. If, however, the force is applied gradually and consistently, the molecules begin to flow irreversibly. (Silly putty, a siloxane polymer, is ideal for demonstrating this effect. If dropped, it bounces; but it can be shaped by the slow application of pressure.) Because of entanglement of the polymer chains and frictional effects, the flowing liquid will be very viscous. This combination of properties, namely elasticity and viscous flow, is why polymers are referred to as viscoelastic materials.

A consequence of viscoelasticity of polymer melt is die swell, which refers to the fact that the thickness of the melt emerging through a narrow orifice or die is greater than the width of the die opening. This is explained as follows: as the molecules flow rapidly through the die opening, they are compressed, and when they emerge, the resultant reduction in pressure causes the molecules to rebound to a degree. This dimensional increase of the extrudate must be taken into account by engineers who design polymer processing machinery ([Chapter 2](#)).

Chain entanglement that contributes to the high viscosity of polymer melt is clearly going to change as the molecular weight increases. Molecular weight is thus a critical variable in polymer rheology. Studies have shown that with flexible chain polymers, there exists a critical molecular weight (\bar{M}_c) for entanglement to begin. For most common polymer, \bar{M}_c falls in the range 4,000–15,000. Although \bar{M}_c varies from one polymer to another, it has been shown that elimination of mass effects arising from substituents on the chains and calculation of chain length leads to a value that is remarkably constant from one polymer to another and corresponds to a \overline{DP} of about 600. In other words, a critical chain length, rather than a critical molecular weight per se, is necessary for entanglement.

1.8 Structural Shape of Polymer Molecules

Polymers can be classified, based on the structural shape of polymer molecules, as linear, branched, or cross-linked. Schematic representations are given in Figure 1.15. Linear polymers have repeating units linked together in a continuous length (Figure 1.15a). When branches protrude from the main polymer chain at irregular intervals, the polymer is termed a branched polymer. Branches may be long or short, forming a comblike structure (Figure 1.15b), or divergent (Figure 1.15c), forming a dendritelike structure. [Regularly repeating side groups which are a part of the monomer structure are not considered as branches. Thus polypropylene is a linear polymer, as are polystyrene and poly(methyl methacrylate).]

Both linear and branched polymers are thermoplastic; that is, they can be softened and hardened reversibly by changing the temperature. Fabricating processes like injection molding, extrusion molding, casting, and blowing take advantage of this feature to shape thermoplastic resins. The rigidity of thermoplastic resins at low temperatures is attributed to the existence of secondary bond forces between the polymer chains. These bonds are destroyed at higher temperatures, thereby causing fluidity of the resin.

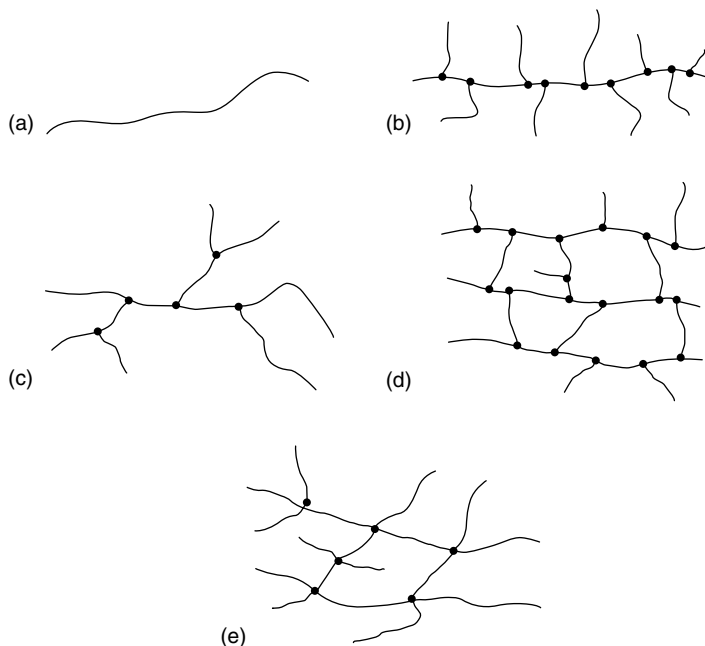


FIGURE 1.15 Schematic representation of (a) linear, (b and c) branched, and (d and e) cross-linked polymers. The branch points and junction points are indicated by heavy dots.

Polymers used as textile fibers are linear. However, they must satisfy two additional requirements: (1) high molecular weight and (2) a permanent orientation of the molecules parallel to the fiber axis. The molecules must have a high degree of order and/or strong secondary forces to permit orientation and crystallization. The chain orientation necessary to develop sufficient strength by crystallization is achieved by a process known as cold drawing, in which the initially formed filaments (unoriented or only slightly oriented) are drawn at a temperature above the glass transition temperature (discussed later), which is the temperature at which sufficient energy is available to the molecular segments to cause them to begin to rotate.

Elastomeric materials, like thermoplastic resins and fibers, are essentially linear polymers. But certain distinctive features in their molecular structure give rise to rubberlike elasticity. Elastomeric polymers have very long chain molecules occurring in randomly coiled arrangements in the unstressed condition. A large deformation is thus possible merely by reorienting the coiled molecules. When elongated, the molecular coils partially open up and become aligned more or less parallel to the direction of elongation. The aligned configuration represents a less probable state or a state of lower entropy than a random arrangement. The aligned polymer chains therefore have a tendency to return to their original randomly coiled state. The large deformability of elastomeric materials is due to the presence of a certain internal mobility that allows rearranging the chain orientation, the absence of which in linear chain plastic materials (at normal temperatures) constitutes the essential difference between the two groups.

Although the aforesaid requirements are necessary conditions for ensuring a large extent of deformability, the remarkable characteristic of the rubbery state—namely, nearly complete recovery—cannot be obtained without a permanent network structure, since permanent deformation rather than elastic recovery will occur. A small amount of cross-linkage is necessary to provide this essential network structure [14,15]. Natural rubber (polyisoprene), for example, simply flows like an extremely viscous liquid at room temperature if it is not cross-linked. Cross-links are introduced into a rubber by heating raw rubber with sulfur (1%–2% by weight) and accelerating agents. Sulfur reacts with the double-bonded carbon atoms to produce a network structure, as shown schematically in [Figure 1.16](#). The amount of cross-linkage must be as small as possible to retain the structure; excessive cross-linkages will make the internal structure too stiff to permit even the required rearrangement of chain orientation during both deformation and recovery—in other words, it will destroy the rubbery state. An example of this is best furnished by ebonite, which is a rigid plastic made by vulcanizing natural rubber with large quantities of sulfur.

Example 2

(a) How much sulfur is required to fully cross-link natural rubber? (b) What is the sulfur content of vulcanized natural rubber that is 50% cross-linked? (Assume that each cross-link contains one sulfur atom).

Answer. Mer weight of isoprene (Figure 1.16a):

$$\text{C}_5\text{H}_8 = (5)(12) + (8)(1) = 68 \text{ g/mer}$$

Assuming $x = 1$ in Figure 1.16b, one sulfur atom, on the average, is required for cross-linking per mer of isoprene. Therefore,

$$(a) \text{ Amount of sulfur} = (32/68)100 = 47 \text{ g/100 g of raw rubber}$$

$$(b) \text{ Sulfur content} = 100(0.5)(32)/[0.5(32) + 68] = 19\%$$

Example 3

A rubber contains 60% butadiene, 30% isoprene, 5% sulfur, and 5% carbon black. What fraction of possible cross-links are joined by vulcanization? (Assume that all the sulfur is used in cross-linking.)

Answer. 1 mer weight of butadiene (C_4H_6) = $(4)(12) + (6)(1) = 54 \text{ g/mer}$

$$1 \text{ mer weight of isoprene } (\text{C}_5\text{H}_8) = (5)(12) + (8)(1) = 68 \text{ g/mer}$$

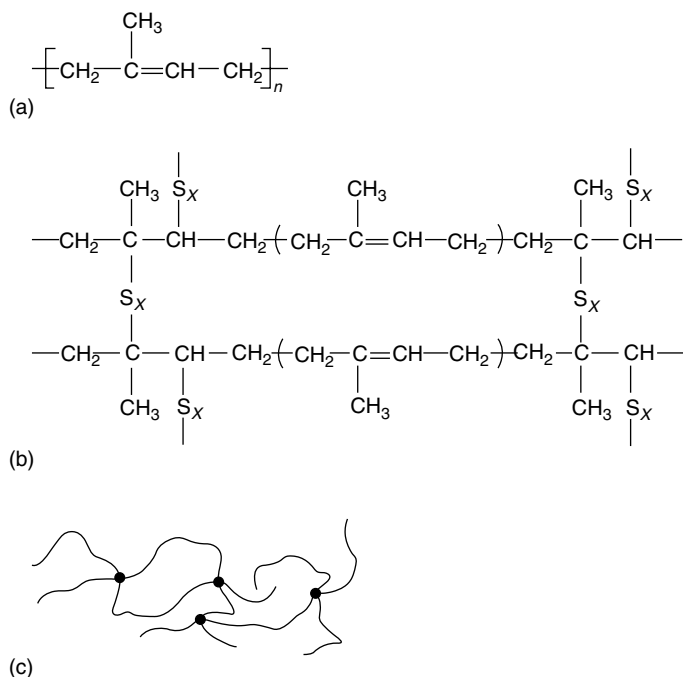


FIGURE 1.16 Vulcanization of natural rubber with sulfur. (a) Linear polyisoprene (natural rubber). (b) Vulcanized structure (idealized) showing cross-links of sulfide groups. The number, x , of sulfur atoms in a cross-link is 1 or 2 in efficient vulcanization systems but may be as high as 8 under conditions where cyclic and other structures are also formed in the reaction. (c) The effect of cross-linking is to introduce points of linkage or anchor points between chain molecules, restricting their slippage. The cross-links in elastomers are typically a few hundred carbon atoms apart.

1 atomic weight of sulfur = 32. Assuming that, on the average, one sulfur atom per mer is required for cross-linking, we get

$$\text{Fraction of cross-links} = \frac{5/32}{60/54 + 30/68} = 0.101 \text{ or } 10.1\%$$

1.9 Thermal Transitions in Polymers

The term “transition” refers to a change of state induced by changing the temperatures or pressure. Two major thermal transitions are the glass transition and the melting, the respective temperatures being called T_g and T_m .

1.9.1 T_g and T_m

All polymers are hard rigid solids at sufficiently low temperatures, but as the temperature rises a thermoplastic polymer eventually acquires sufficient thermal energy to enable its chains to move freely enough for it to behave like a viscous liquid (assuming there is no degradation). There are several ways in which a polymer can pass from the solid to the liquid phase, depending on the structure of the polymer chains and their arrangement in the sample. The different types of thermal response in this transition from a rigid solid to an eventually liquid state can be illustrated in several ways. One of the simplest and most satisfactory is to trace the change in specific volume, as shown schematically in [Figure 1.17](#).

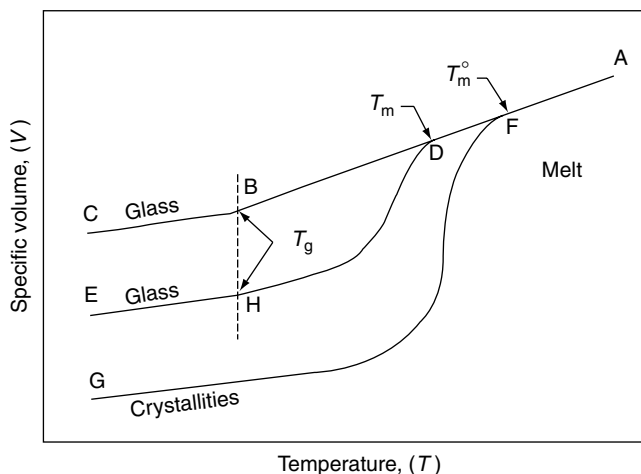


FIGURE 1.17 Schematic representation of the change of specific volume of a polymer with temperature for a completely amorphous sample (A–B–C), a semicrystalline sample (A–D–E), and a perfectly crystalline material (A–F–G).

In first-order transitions, such as melting, there is a discontinuity in the volume–temperature plot (Figure 1.17) or enthalpy–temperature plot at the transition temperature. In second-order transitions, only a change in slope occurs and thus there is a marked change in the first derivative or temperature coefficients, as illustrated in Figure 1.18. The glass transition is not a first-order transition, as no discontinuities are observed at T_g when the specific volume or entropy of the polymer is measured as a

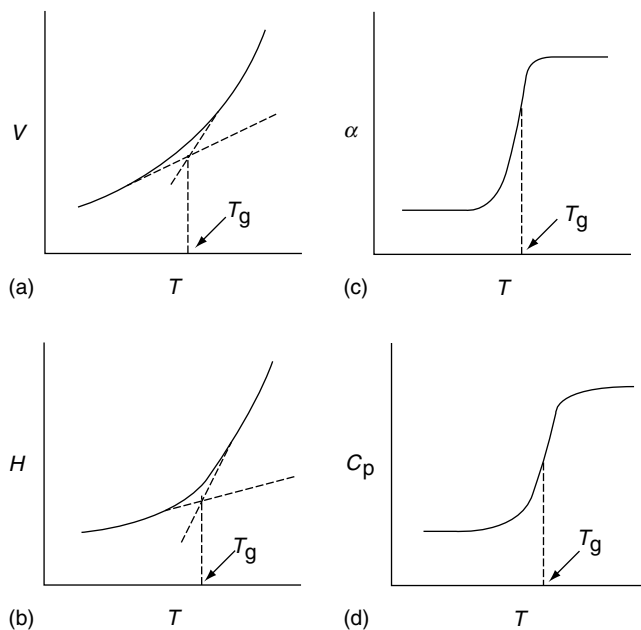


FIGURE 1.18 Idealized variations (a,b) in volume (V) and enthalpy (H). Also shown (c,d) are α , the volume coefficient of expansion, and C_p , the heat capacity, which are, respectively, the first derivatives of V and H with respect to temperature (T).

function of temperature. However, the first derivative of the property–temperature curve, i.e., the temperature coefficient of the property, exhibits a marked change in the vicinity of T_g ; for this reason it is sometimes called a second-order transition.

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (1.26)$$

where V is the volume of the material, and α has the units K^{-1} . While this quantity increases rather sharply at T_g , the increase actually occurs over a range ($10^\circ C$ – $30^\circ C$). Similar changes occur in the heat capacity at constant pressure (C_p), which is the first derivative of enthalpy H with respect to temperature.

A thermoplastic polymer may be completely amorphous in the solid state, which means that the polymer molecular chains in the specimen are arranged in a totally random fashion. Referring to Figure 1.17, the volume change in amorphous polymers follows the curve ABC. In the region C–B, the polymer is a glassy solid and has the characteristics of glasses, including hardness, stiffness and brittleness. In the glassy region, the available thermal energy (RT energy units/mol) is insufficient to allow rotation about single bonds in the polymer backbone overcoming intramolecular energy barriers, and movements of large (some 10–50 consecutive chain atoms) segments of the polymer chain cannot take place. But as the sample is heated, it passes through a temperature T_g , called the glass transition temperature, above which it softens and becomes rubberlike. This is an important temperature and marks the onset of extensive molecular motion which is reflected in marked changes in properties, such as specific volume, refractive index, stiffness, and hardness. Above T_g , the material may be more easily deformed or become ductile. A continuing increase in temperature along B–A leads to a change of the rubbery polymers to a viscous liquid without any sharp transition.

In a perfectly crystalline polymer, all the chains would be contained in regions of three-dimensional order, called crystallites, and no glass transition would be observed, because of the absence of disordered chains in the sample. A perfectly crystalline polymer, on heating, would follow curve G–F–A, melting at T_m° to become a viscous liquid.

Perfectly crystalline polymers are, however, not encountered in practice and real polymers may instead contain varying proportions of ordered and disordered regions in the sample. These semicrystalline polymers usually exhibit both T_g and T_m (not T_m°) corresponding to the disordered and ordered regions, respectively, and follow curves similar to E–H–D–A. As T_m° is the melting temperature of a perfectly crystalline polymer of high molecular weight T_m is lower than T_m° and more often represents a melting range, because the semicrystalline polymer contains crystallites of various sizes with many defects which act to depress the melting temperature.

Both T_g and T_m are important parameters that serve to characterize a given polymer. While T_g sets an upper temperature limit for the use of amorphous thermoplastics like poly(methyl methacrylate) or polystyrene and a lower temperature limit for rubbery behavior of an elastomer like SBR rubber or 1,4-*cis*-polybutadiene, T_m or the onset of the melting range determines the upper service temperature. Between T_m and T_g , semicrystalline polymers tend to behave as a tough and leathery material. As a general rule, however, semicrystalline polymers are used at temperatures between T_g and a practical softening temperature which lies above T_g and below T_m . (The onset of softening is usually measured as the temperature required for a particular polymer to deform a given amount under a specified load. These values are known as heat deflection temperatures. Such data do not have any direct relations with T_m , but they are widely used in designing with plastics.)

The T_g and T_m values for some polymers are shown in Table 1.5. In general, both T_g and T_m are affected in the same manner by considerations of polymer structure [16]. Thus, both T_g and T_m increase with higher molecular symmetry, structural rigidity, and secondary forces of polymer chains.

The T_g and T_m values of a polymer determine the temperature range in which it can be employed. Amorphous elastomeric polymers, for example, must be used at temperatures (region B–D in Figure 1.17) well above T_g to permit the high, local segmental mobility required in such materials. Thus styrene–butadiene (25/75) copolymer ($T_g = -57^\circ C$), polyisoprene ($T_g = -73^\circ C$), and

TABLE 1.5 Glass Transition Temperatures (T_g) and Crystalline Melting Temperatures (T_m) of Polymers

Polymer	T_g (°C)	T_m (°C)
Polyethylene (high density)	−115	137
Polyoxymethylene	−85	181
Polyisoprene (natural rubber)	−73	28
Polyisobutylene	−73	44
Polypropylene	−20	176
Poly(vinylidene chloride)	−19	190
Poly(chlorotrifluoroethylene) (kel-F)	45	220
Poly(hexamethylene adipamide) (nylon-6,6)	53	265
Poly(ethylene terephthalate) (Terylene, Dacron)	69	265
Poly(vinyl chloride)	81	212
Polystyrene	100	240
Poly(methyl methacrylate) (Perspex, Lucite)	105	200
Cellulose triacetate	105	306
Polytetrafluoroethylene (Teflon)	127	327

polyisobutylene ($T_g = -73^\circ\text{C}$) can be used as rubbers at ambient temperatures. Amorphous structural polymers, such as polystyrene and poly(methyl methacrylate), depend on their glasslike rigidity below T_g for their utility; they should therefore have high T_g values so that under ambient conditions they are well below T_g .

Tough, leatherlike polymers are limited for use in the immediate vicinity of their T_g . Such behavior is observed in vinyl chloride-based plastics, which are used as substitutes for leather in automobile seat covers, travel luggage, and ladies' handbags. Highly crystalline fiber-forming polymers must be used at temperatures substantially below T_m (about 100°C), since changes in crystal structure can occur as T_m is approached. The T_m of a fiber must therefore be above 200°C to remain unaffected at use temperatures encountered in cleaning and ironing. (T_m should not, however, be excessively high—not more than 300°C ; otherwise spinning of the fiber by melt-spinning processes may not be possible.) The T_g of a fiber, on the other hand, should have an intermediate value, because too high a value of T_g would interfere with the stretching operation as well as with ironing, and too low a value of T_g would not permit crease retention in fabrics. Nylon and terylene, as may be seen from Table 1.5, therefore have optimal values of T_m and T_g . Semicrystalline polymers with about 50% crystallinity are used at temperatures between T_g and T_m , since in this range the material exhibits moderate rigidity and a high degree of toughness, somewhat analogous to reinforced rubber. Branched polyethylene (low density), with $T_g = -120^\circ\text{C}$ and $T_m = 115^\circ\text{C}$, used at ambient temperatures is a typical example.

1.9.2 Regions of Viscoelastic Behavior

As we have seen above, the transition that separates the glassy state from the viscous state is known as the glass–rubber transition. This transition attains the properties of a second-order transition at very slow rates of heating or cooling. In order to clearly locate the region of this transition and to provide a broader picture of the temperature dependence of polymer properties, the principal regions of viscoelastic behavior of polymers will be briefly discussed.

Broadly, there are five regions of viscoelastic behavior for linear amorphous polymers as shown in Figure 1.19. In region I (a–b), the polymer is glassy and frequently brittle. Typical examples are polystyrene and poly(methyl methacrylate) at room temperature. Young's modulus in this region just below the glass transition temperature is approximately 3×10^{10} dyne/cm² (3×10^9 Pa) and it is nearly the same for a wide range of polymers.

Range II (b–c) is the glass transition region. Typically, the modulus drops a factor of about a thousand in a 20°C – 30°C range. The behavior of polymers in this region is best described as leathery. For static or quasistatic measurements, such as illustrated in Figure 1.19, the glass transition temperature, T_g , is often

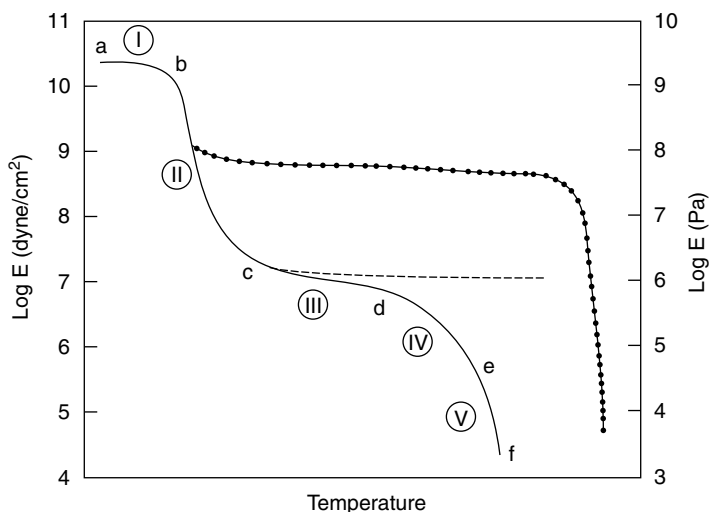


FIGURE 1.19 Five regions of viscoelastic behavior for a linear, amorphous polymer: I (a–b), II (b–c), III (c–d), IV (d–e), and V (e–f). Also illustrated are effects of crystallinity (dotted line) and cross-linking (dashed line).

taken at the maximum rate of turndown of the modulus at the elbow, i.e., where d^2E/dT^2 is at a maximum. A few T_g values are shown in Table 1.5.

Region III (c–d) in Figure 1.19 is the rubbery plateau region. After a sharp drop that the modulus exhibits in the glass transition region, it again becomes almost constant in the rubbery plateau region, with typical values of 2×10^7 dyne/cm² (2×10^6 Pa). In this region, polymers exhibit high rubber elasticity, so much so that an elastomer in this region can be stretched perhaps several hundred percent and substantially snap back to its original length on being released.

In region III (c–d) of Figure 1.19, two cases need be distinguished. First, if the polymer is linear, the solid line is followed on which the modulus drops off slowly with increasing temperature. The width of the plateau is governed primarily by the molecular weight of the polymer; the higher the molecular weight, the longer the plateau. Second, if the polymer is cross-linked, the dashed line in Figure 1.19 is followed, and improved rubber elasticity is observed, with the creep portion suppressed. A common example of a cross-linked polymer above its glass transition temperature is the ordinary rubber band. For cross-linked polymers, region III remains in effect at higher temperatures up to the decomposition temperature, and regions IV and V do not occur.

[The discussion above has been limited to amorphous polymers. However, if the polymer is semicrystalline, the dotted line in Figure 1.19 is followed. Since the crystalline regions in the polymer matrix tend to behave as a filler phase and also as a type of physical cross-link between the chains, the height of the plateau (i.e., the modulus) will be governed by the degree of crystallinity.]

In the case of linear amorphous polymers, raising the temperature past the rubbery plateau region brings them to the rubbery flow region—region IV. In this region, the polymer exhibits both rubber elasticity and flow properties depending on the time scale of the experiment. For experiments performed in a short time, the physical entanglements of polymer chains are not able to relax and the material still behaves rubbery. For longer-duration experiments, the increased molecular motion imparted by the increased temperature cause chains to move, resulting in visible flow. An example of a material in the rubbery flow region at ambient temperature is Silly Putty which bounces like a ball when thrown (quick experiment) but deforms like a taffy when pulled (a much slower experiment).

Region V (e–f) in Figure 1.19 is the liquid flow region which is reached at still higher temperatures where the increased kinetic energy of the chains permits them wriggle out through entanglements rapidly

and move as individual molecules, often producing highly viscous flow. This is the melting temperature and it is always above the glass transition temperature.

Example 4

A new polymer was reported to soften at 60°C but it is not known for sure whether the softening was a glass transition or a melting point. Describe a simple experiment to distinguish between the two possibilities. It is known however, that the new polymer is essentially a linear polymer.

Answer. If 60°C is a glass transition, then heating the polymer slowly past 60°C would take it to the rubbery plateau region (region III in Figure 1.19), where the modulus E , and hence hardness would remain fairly constant with increase of temperature. For a melting transition, however, the modulus would drop rapidly and the polymer would become increasingly softer in a similar experiment.

Pressing one's thumb in an object is a simple way to gauge the object's hardness. Its scientific analog is the measurement of hardness by indentation. In practice, the point of a weighted needle is allowed to rest on the polymer surface as the temperature is raised. The movement of the needle as it penetrates the surface can be monitored by means of an amplification gauge. Though less accurate than other more sophisticated methods, it is useful for the preliminary engineering-oriented examination of systems.

1.9.3 Factors Affecting T_g

As T_g marks the onset of molecular motion, a number of factors which affect rotation about links (necessary for movement of polymer chains) will also influence the T_g of a polymer. These include (a) chain flexibility, (b) molecular structure (steric effects), (c) molecular weight, and (d) branching and cross-linking.

1.9.3.1 Chain Flexibility

The flexibility of the chain is undoubtedly the most important factor influencing the T_g of a polymer. The chain flexibility depends more on the rotation or torsion of skeletal bonds than on changes in bond angles. When a randomly coiled chain is pulled out into an elongated conformation, the skeletal bonds “unwind” rather than undergo angular distortion (see Figure 1.20). Thus, flexibility on a macroscopic scale depends on torsional mobility at the molecular level. If a highly flexible chain is present, T_g will generally be low and if the chain is rigid, the T_g value will be high.

For symmetrical polymers, the chemical nature of the backbone chain is the important factor determining the chain flexibility and hence T_g . Chains made up of bond sequences that are able to rotate easily are flexible, and hence polymers containing $-(\text{CH}_2-\text{CH}_2)-$, $-(\text{CH}_2-\text{O}-\text{CH}_2)-$, or $-(\text{Si}-\text{O}-\text{Si})-$ links will have correspondingly low values of T_g . For example, poly(dimethyl siloxane) has one of the lowest T_g values known (-123°C) presumably because the Si-O bonds have considerable torsional mobility.

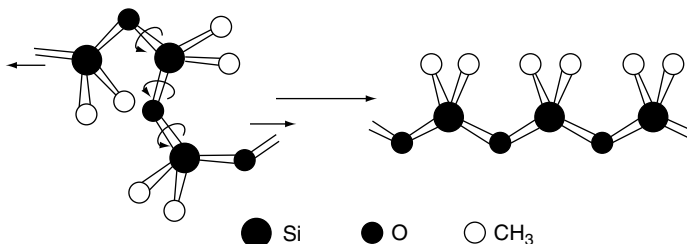
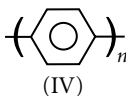
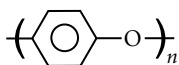


FIGURE 1.20 Elasticity of a polymer such as silicone rubber depends on the ease with which a random coil chain can be stretched out. The stretching is a consequence of the *unwinding* of bonds rather than a marked widening of bond angles.

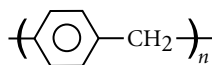
The value of T_g is raised markedly by the insertion of groups that stiffen the chain by impeding rotation, so that more thermal energy is required to set the chain in motion. Particularly effective in this respect is the *p*-phenylene ring. Thus, a chain consisting entirely of *p*-phenylene rings, namely, poly(*p*-phenylene) (IV)



has a highly intractable, rigid structure with no softening point. This structure can be modified by introducing flexible groups in the chain to produce tractable polymers with high values of T_g . Some examples are poly(phenylene oxide) (V), $T_g = 83^\circ\text{C}$ and poly(*p*-xylylene) (VI), $T_g = 280^\circ\text{C}$ as compared to polyethylene, $T_g = -93^\circ\text{C}$, and poly(ethylene oxide), $T_g = -67^\circ\text{C}$.



(V)



(VI)

1.9.3.2 Steric Effects

When the polymer chains are unsymmetrical, with repeat units of the type $-(\text{CH}_2\text{---CHX})-$, an additional restriction is imposed by steric effects depending on the size of the pendant group X. Bulky pendant groups hinder the rotation about the backbone and cause T_g to increase. There is some evidence of a correlation between T_g and the size of the pendant group measured by its molar volume V_X . For example, T_i ($^\circ\text{C}$) increases with increasing V_X (cm^3/mol) in the progressive series, polyethylene ($T_g = -93$, $V_X = 3.7$), polypropylene ($T_g = -20$, $V_X = 25.9$), polyisobutylene ($T_g = 100$, $V_X = 92.3$), and poly(vinylnaphthalene) ($T_g = 135$, $V_X = 143.9$).

Superimposed on the pendant group size factor are the effects of polarity and the intrinsic flexibility of the pendant group itself. Greater intermolecular interactions due to polar groups hinder molecular motion and increase T_g . Thus polar groups tend to encourage a higher T_g than nonpolar groups of similar size, as seen when comparing T_g ($^\circ\text{C}$) and V_X (cm^3/mol) of polypropylene ($T_g = -20$, $V_X = 25.9$), poly(vinyl chloride) ($T_g = 81$, $V_X = 22.1$), and polyacrylonitrile ($T_g = 105$, $V_X = 30.0$). On the other hand, greater flexibility of side chain leads to lower T_g as is evident on examination of the polyacrylate series from methyl through butyl: poly(ethylacrylate) ($T_g = -24$, $V_X = 82.3$), poly(propyl acrylate) ($T_g = -48$, $V_X = 104.5$), and poly(butyl acrylate) ($T_g = -55$, $V_X = 126.7$), where T_g is in $^\circ\text{C}$ and V_X is in cm^3/mol .

A further increase in steric hindrance is caused by the presence of an α -methyl group, which restricts rotation even further, thus causing T_g to increase. Typical examples are the pair polystyrene ($T_g = 100^\circ\text{C}$)–poly(α -methylstyrene) ($T_g = 172^\circ\text{C}$) and the pair poly(methyl acrylate) ($T_g = 6^\circ\text{C}$)–poly(methyl methacrylate) ($T_g = 105^\circ\text{C}$).

1.9.3.3 Configurational Effects

It should be noted that the steric effects of the pendant groups considered above are simply additional contributions to the main chain effects. Similarly *cis*–*trans* isomerism in polydienes and tacticity variations in certain α -methyl substituted polymers alter chain flexibility and hence affect T_g . Well-known examples of *cis*–*trans* variations are polybutadiene *cis* ($T_g = -108^\circ\text{C}$) and *trans* ($T_g = -18^\circ\text{C}$) or polyisoprene *cis* ($T_g = -73^\circ\text{C}$) and *trans* ($T_g = -53^\circ\text{C}$). An example of tacticity variation is poly(methyl methacrylate) for which the isotactic, atactic, and syndiotactic stereostructures are associated with T_g values of 45, 105, and 115°C , respectively.

1.9.3.4 Effect of Cross-Linking

When cross-links are introduced into a polymer, the molecular motion in the sample is restricted and T_g rises. This transition is ill-defined for a high cross-link density, but at lower values T_g is found to increase linearly with the number of cross-links.

1.9.4 Factors Affecting T_m

The application of macroscopic thermodynamics leads to some useful generalizations of factors affecting T_m . At T_m , the free energy change is zero, i.e.,

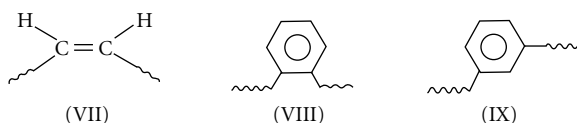
$$\Delta G_m = \Delta H_m - T_m \Delta S_m = 0$$

where $T_m = \Delta H_m / \Delta S_m$. This expression for T_m predicts that a high melting point can be the result of a high value of the enthalpy change ΔH_m and/or a small value of the entropy change ΔS_m in melting. The former corresponds to stronger binding of adjacent but unbonded units in the polymer lattice and thus to higher degree of crystallinity. The factors that affect crystallinity and T_m can be classified as symmetry, intermolecular bonding, tacticity, branching, and molecular weight. These are discussed below. If ΔS_m is small, melting does not result in a large gain of conformational entropy and, to some degree, the structure of the solid must persist in the melt. For example, molecules of isotactic polypropylene crystallize in the form of helices and these are thought to occur in the melt as well, thus making ΔS_m small and T_m high.

1.9.4.1 Symmetry

The formation of stable crystalline regions (crystallites) in a polymer requires (a) that an efficient close-packed arrangement of the polymer chains can be achieved in three dimensions and (b) that a favorable change in internal energy is obtained during this process. This imposes restrictions on the type of chain that can form crystallites easily and one would expect linear chains with high degree of symmetry such as polyethylene, polytetrafluoroethylene, various polyesters, and polyamides to crystallize most readily.

Linear symmetrical molecules such as polyethylene, polytetrafluoroethylene, and other linear molecules with more complex backbones containing $-(O)-$, $-(COO)-$, and $-(CONH)-$ groups, such as polyethers, polyesters, and polyamides, all possess a suitable symmetry for crystallite formation and usually assume extended zigzag conformations when aligned in the lattice. On the other hand, chains containing irregular units, which impair the symmetry, reduce the ability of the polymer to crystallize. Thus *cis* double bonds (VII), *o*-phenylene groups (VIII), and *m*-phenylene groups (IX) all encourage bending and twisting in the chains and make close packing very difficult.



If, however, the phenylene rings are para-oriented, the chains retain their axial symmetry and can crystallize more readily. Similarly, double bonds in *trans* configuration maintain the chain symmetry thus allowing for crystallite formation. This is highlighted by a comparison of the amorphous elastomeric *cis*-polyisoprene ($T_m = 28^\circ\text{C}$) with highly crystalline *trans*-polyisoprene ($T_m = 74^\circ\text{C}$), which is a nonelastomeric rigid polymer, or *cis*-1,4-polybutadiene ($T_m = -11^\circ\text{C}$) with *trans*-1,4-polybutadiene ($T_m = 148^\circ\text{C}$).

Another aspect of high chain symmetry is the possibility of molecular motion within the crystal lattice contributing to higher T_m . For example, polyethylene and polytetrafluoroethylene are both sufficiently symmetrical to be considered as smooth, stiff cylindrical rods. In the crystal, these rods tend to roll over each other and change position when thermally agitated. This motion within the crystal lattice, called premelting, effectively stabilizes the lattice. Consequently, more thermal energy is required to break down

the crystallite into a disordered melt, and T_m is raised. Irregularly shaped polymers with bends and bumps in the chain cannot move in this way without disrupting the crystal lattice, and so have lower T_m values.

1.9.4.2 Intermolecular Bonding

Any interaction between polymer chains in the crystal lattice serves to hold the structure more firmly and raise the melting temperature. In polyethylene, the close packing in crystallites achieved due to high chain symmetry and lack of substituents on the chains allows the van der Waals forces to act cooperatively and provide additional stability to the lattice. In polymers containing polar substituents, for example, Cl, CN, or OH, the chains can be aligned and held rigidly by the strong dipole-dipole interactions between the substituents. This effect is more obvious in the symmetrical polyamides. These polymers can form intermolecular hydrogen bonds which greatly enhance crystallite stability and raise the T_m significantly.

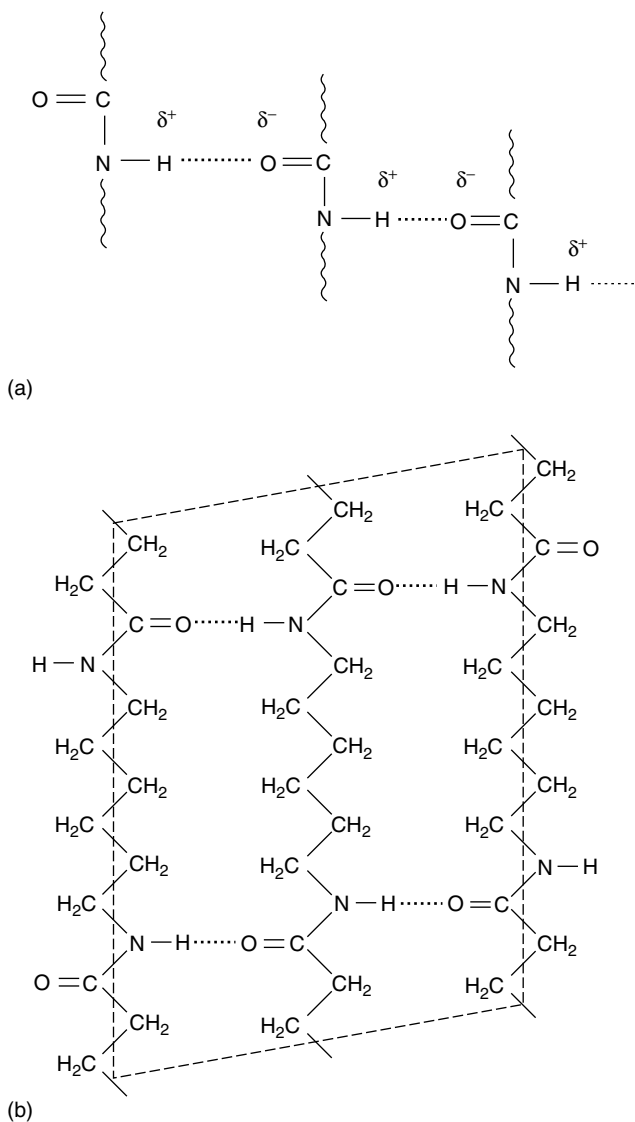


FIGURE 1.21 (a) Hydrogen bonds between neighboring chains of polyamide. (b) Arrangement of chains in hydrogen-bonded sheets in the crystal structure of nylon-6,6.

This is illustrated in [Figure 1.21](#) for nylon-6,6, where the extended zigzag structure greatly facilitates the formation of regular intermolecular hydrogen bonding. The increased stability is reflected in the value of T_m , which for nylon-6,6 is 267°C, compared with 137°C for high-density polyethylene.

1.9.4.3 Tacticity

Stiffening of the polymer chain due to the presence of large pendant groups tends to raise T_m , but this will also increase the difficulty of close packing to form a crystalline array and so tend to lower T_m . However, this latter problem can be overcome if the pendant groups are arranged in a regular fashion along the chain. Thus isotactic polymers tend to form helices to accommodate the substituents in the most stable steric positions, and being of regular forms these helices are capable of regular alignment promoting crystallite formations. Thus isotactic polystyrene is semicrystalline ($T_m = 240^\circ\text{C}$), though atactic polystyrene is amorphous. Syndiotactic polymers are also sufficiently regular to crystallize, not necessarily as a helix, but rather in glide planes.

1.9.4.4 Branching, Chain Flexibility, and Molecular Weight

Chain flexibility has a direct bearing on the melting point. Insertion of groups that stiffen the chain increases T_m , while introducing flexible groups into the chain lowers the value of T_m (see “[Factors Affecting \$T_m\$](#) ”). Branching in the side group tends to stiffen the chain and raise T_m , as shown in the series poly(but-1-ene) ($T_m = 126^\circ\text{C}$), poly(3-methyl but-1-ene) ($T_m = 145^\circ\text{C}$), poly(3,3'-dimethyl but-1-ene) ($T_m > 320^\circ\text{C}$). However, if the side groups are flexible and nonpolar, T_m is lowered. Also, if the chain is substantially branched to reduce the packing efficiency, the crystalline content is lowered, as is the melting point. A good example is low-density polyethylene where extensive branching lowers the density and T_m of the polymer.

Molecular weight in relatively lower order can have significant effect on T_m . Since chain ends are relatively free to move and the number of chain ends increases with the decrease in molecular weight T_m is lowered because less energy is then required to stimulate chain motion and melting. For example, polypropylene with molecular weight 2,000 has $T_m = 114^\circ\text{C}$, whereas a sample with molecular weight 30,000 has $T_m = 170^\circ\text{C}$.

1.9.5 Relation between T_m and T_g

While T_m is a first-order transition, T_g is a second-order transition and this precludes the possibility of a simple relation between them. There is, however, a crude relation between T_m and T_g . Thus the ratio T_g/T_m range from 0.5 to 0.75 when the temperatures are expressed in Kelvin. The relation is represented in [Figure 1.22](#) where a broad band covers most of the results for linear homopolymers and the ratio (T_g/T_m) lies between 0.5 and 0.75 for about 80% of these [17,18]. The ratio is closer to 0.5 for symmetrical polymers such as polyethylene and polybutadiene, but closer to 0.75 for unsymmetrical polymers, such as polystyrene and polyisoprene. The difference in these values may be related to the fact that in unsymmetrical chains with repeat units of the type $-(\text{CH}_2-\text{CHX})-$ an additional restriction to rotation is imposed by steric effects causing T_g to increase, and conversely, an increase in symmetry lowers T_g .

1.10 Designing a Polymer Structure for Improved Properties

The three principles [19] applied to give strength and resistance to polymers are (1) crystallization, (2) cross-linking, and (3) increasing inherent stiffness of polymer molecules. Combinations of any two or all of the three strengthening principles have proved effective in achieving various properties with polymers ([Figure 1.23](#)). For polymers composed of inherently flexible chains, crystallization and cross-linking are the only available means to enhance polymer properties. The factors affecting the crystallinity of polymers have been discussed previously, and the methods of introducing cross-links between polymer molecules are discussed later.

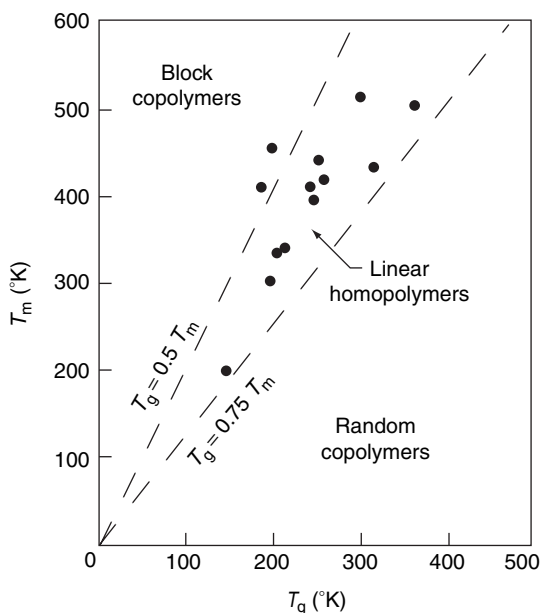


FIGURE 1.22 Plot of T_m against T_g for linear homopolymers with T_g/T_m in the range 0.5 and 0.75 broadly demarcating $T_m - T_g$ domains covered by homopolymers and copolymers.

The third, and relatively new, strengthening principle is to increase chain stiffness. One possible way of stiffening a polymeric chain is to hang bulky side groups on the chain to restrict chain bending. For example, in polystyrene, benzene rings are attached to the carbon backbone of the chain; this causes stiffening of the molecule sufficient to make polystyrene a hard and rigid plastic with a softening temperature higher than that of polyethylene, even though the polymer is neither cross-linked nor crystalline. The method is advantageous because the absence of crystallinity makes the material completely transparent, and the absence of cross-linking makes it readily moldable. A similar example is poly(methyl methacrylate).

However, the disadvantage of attaching bulky side groups is that the material dissolves in solvents fairly easily and undergoes swelling, since the bulky side groups allow ready penetration by solvents and swelling agents. This problem can be eliminated by stiffening the backbone of the chain itself. One way to do this is to introduce rigid ring structures in the polymer chain. A classic example of such a polymer is cellulose, which is the structural framework of wood and the most abundant organic material in the world. Its chain molecule consisting of a string of ring-shaped condensed glucose molecules has an intrinsically stiff backbone. Cellulose therefore has a high tensile strength. In poly(ethylene terephthalate) fiber the chains are only moderately stiff, but the combination of chain stiffness and crystallization suffices to give the fiber high strength and a high melting point (265°C). The new plastic polycarbonate containing benzene rings in the backbone of the polymer chain (Table 1.3) is so tough that it can withstand the blows of a hammer. Ladder polymers based on aromatic chains consist of double-stranded chains made up of benzene-type rings [20]. These hard polymers are completely unmeltable and insoluble.

The combination of all three principles has led to the development of new and interesting products with enhanced properties. Composites based on epoxy and urethane-type polymers may be cited as an example. Thus, the stiff polymeric chains of epoxy and urethane types are cross-linked by curing reactions, and fillers are added to produce the equivalent of crystallization.

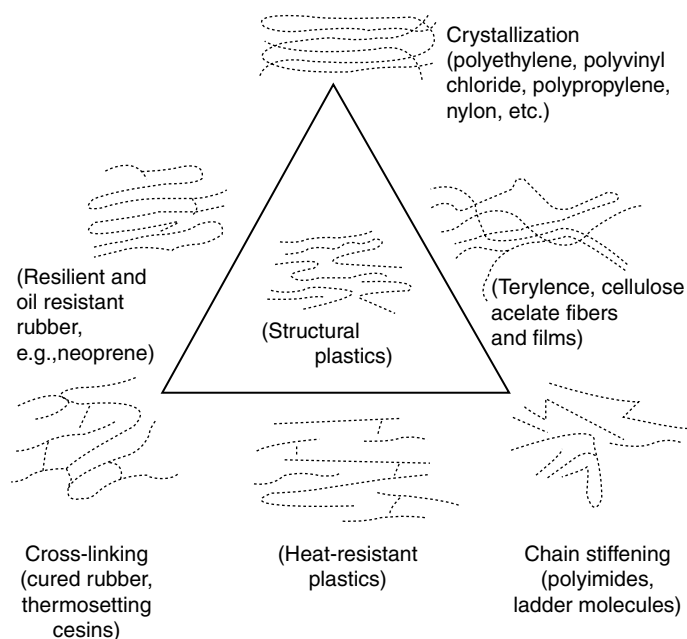


FIGURE 1.23 Three basic principles—crystallization, cross-linking, and chain stiffening—for making polymers strong and temperature resistant are represented at the three corners of the triangle. The sides and the center of the triangle indicate various combinations of the principles. (After Mark, H. F. 1967. *Sci. Am.*, 217, 3, Sept. 19, 148, see also p. 156.)

1.11 Cross-Linking of Polymer Chains

Cold flow can be prevented by cross-links between the individual polymer chains. The structure of polymer chains present in the cross-linked polymers is similar to the wire structure in a bedspring, and chain mobility, which permits one chain to slip by another (which is responsible for cold flow) is prevented. Natural rubber, for example, is a sticky product with no cross-linking, and its polymer chains undergo unrestricted slippage; the product has limited use. However, as we have seen, when natural rubber is heated with sulfur, cross-linking takes place (Figure 1.16). Cross-linking by sulfur at about 5% of the possible sites gives rubber enough mechanical stability to be used in automobile tires but still enables it to retain flexibility. Introducing more sulfur introduces more cross-links and makes rubber inflexible and hard.

Cross-linking of polymer chains can be brought about by (1) reactions of functional groups; (2) vulcanization, using peroxides, sulfur, or sulfur-containing compounds; (3) free-radical reactions caused by ionizing radiation; (4) photolysis involving photosensitive functional groups; or (5) coulombic interactions of ionic species.

1.11.1 Reactions of Functional Groups

Cross-linking by chemical reactions is an important process in polymer technology. A few common examples of cross-linking involving prepolymers are illustrated in Figure 1.24 through Figure 1.30. The cross-links are usually formed between prepolymer molecules by foreign molecules [e.g., styrene in unsaturated polyesters (Figure 1.28)] or by small chain segments, as in phenolic resin (Figure 1.24) and glyptal resin (Figure 1.30).

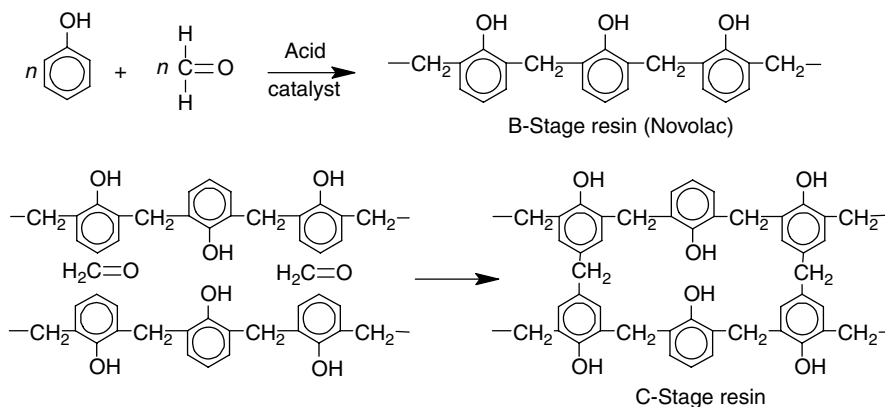


FIGURE 1.24 Equations (idealized) for the production of phenol-formaldehyde resins.

A high degree of cross-linking gives rise to three-dimensional or space network polymers in which all polymer chains are linked to form on giant molecule. Thus, instead of being composed of discrete molecules, a piece of highly cross-linked polymer constitutes, essentially, just one molecule. At high degree of cross-linking, polymers acquire rigidity, dimensional stability, and resistance to heat and chemicals [15]. Because of their network structure such polymers cannot be dissolved in solvents and cannot be softened by heat; strong heating only cause decomposition. Polymers or resins which are transformed into a cross-linked product, and thus take on a set on heating, are said to be of thermosetting type. Quite commonly, these materials are prepared, by intent, in only partially polymerized states (prepolymers), so that they may be deformed in the heated mold and then hardened by curing (cross-linking).

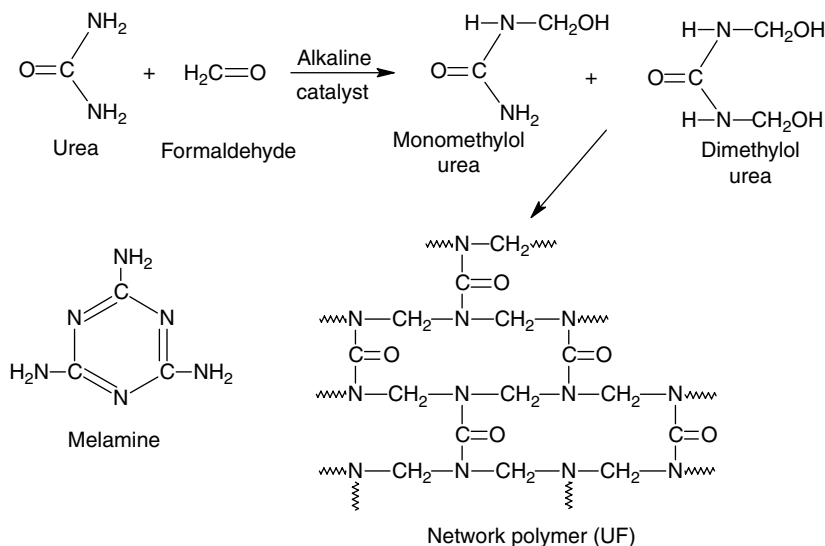


FIGURE 1.25 The two important classes of amino resins are the products of condensation reactions of urea and melamine with formaldehyde. Reactions for the formation of urea-formaldehyde amino resins (UF) are shown. Preparation of melamine-formaldehyde resins is similar.

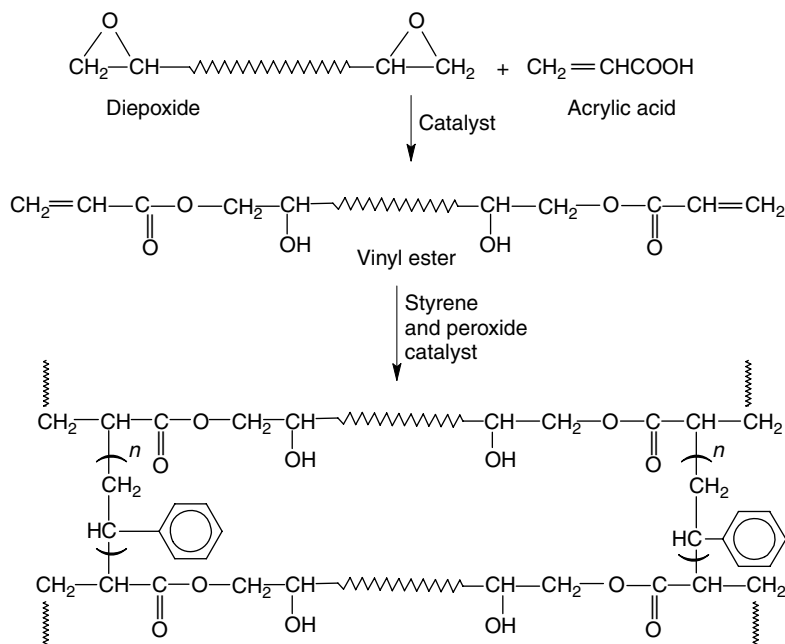
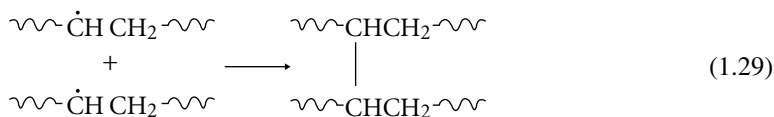
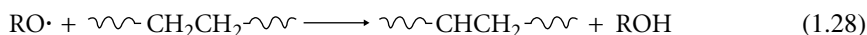


FIGURE 1.27 Equations for the preparation of a vinyl ester.

1.11.2 Vulcanization

Vulcanization is a general term applied to cross-linking of polymers, particularly elastomers. Many polymers are cross-linked by compounding with a peroxide such as dicumyl peroxide or di-*t*-butyl peroxide and then heating the mixture. Peroxide-initiated cross-linking of saturated polymers such as polyethylene proceeds by hydrogen abstraction (Equation 1.28) by radicals resulting from hemolytic cleavage of peroxide (Equation 1.27), followed by radical combination (Equation 1.29):



With unsaturated polymers, hydrogen abstraction probably occurs at the allylic position (Equation 1.30) with subsequent cross-linking again resulting from radical combination (Equation 1.31).



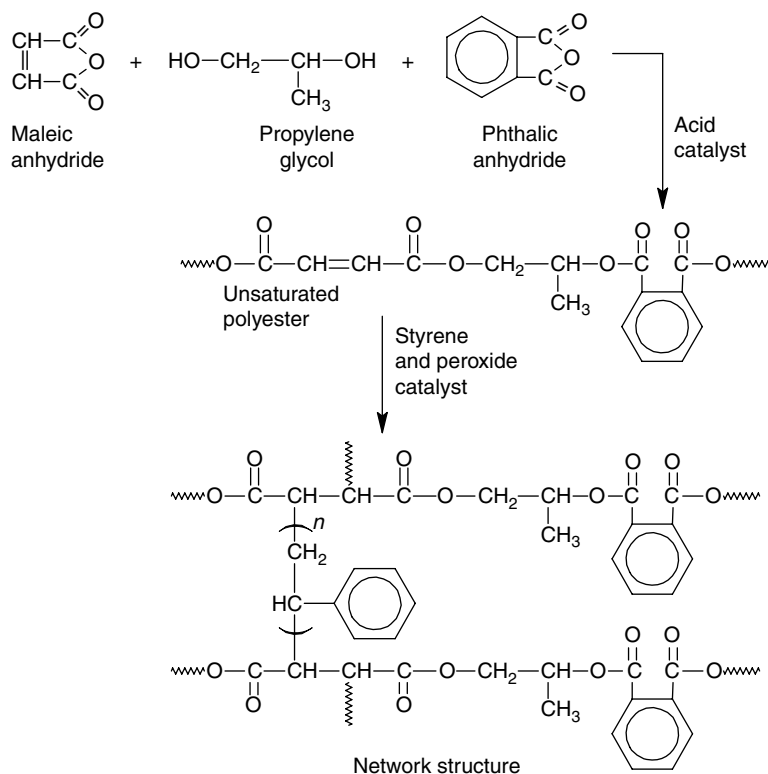
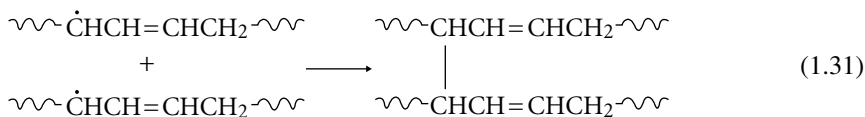
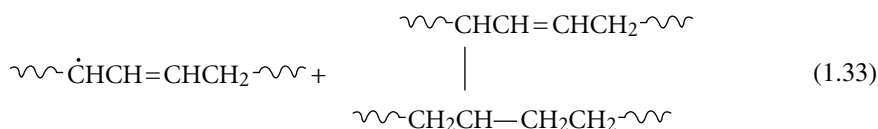
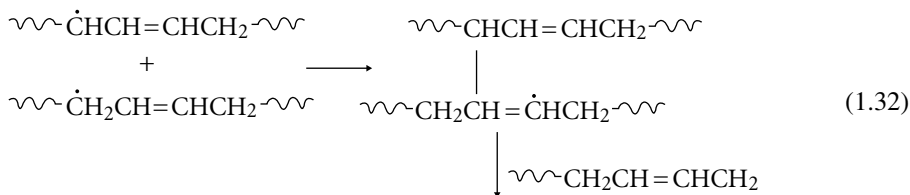


FIGURE 1.28 Equations for preparation and curing of an unsaturated polyester resin. The presence of ethylenic unsaturation provides sites for cross-linking by a chain reaction mechanism in the presence of styrene. Phthalic anhydride increases flexibility by increasing spacing of cross-links.



Moreover, addition-transfer processes (Equation 1.32 and Equation 1.33) can also cause cross-linking, because in many instances considerably more cross-links are formed than would be expected on the basis of only abstraction-combination reactions described above.



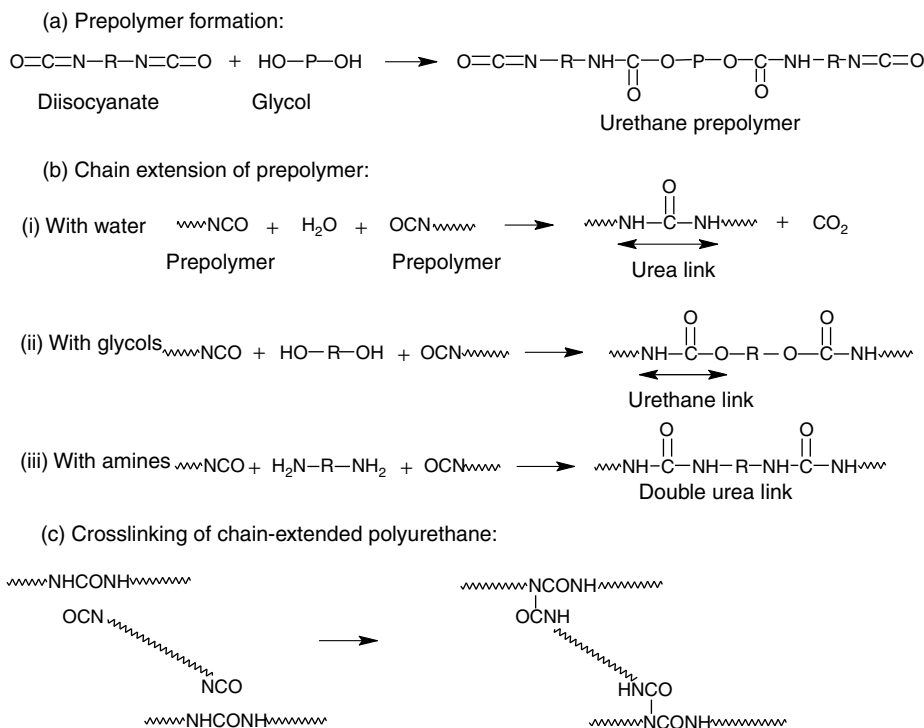


FIGURE 1.29 Equations for preparation, chain extension, and curing of polyurethane.

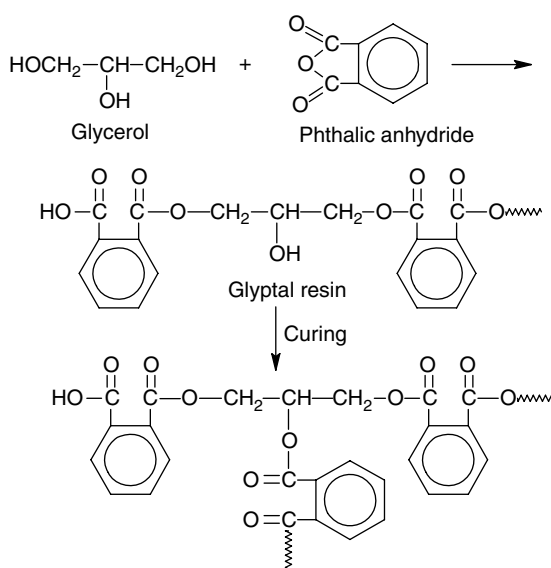
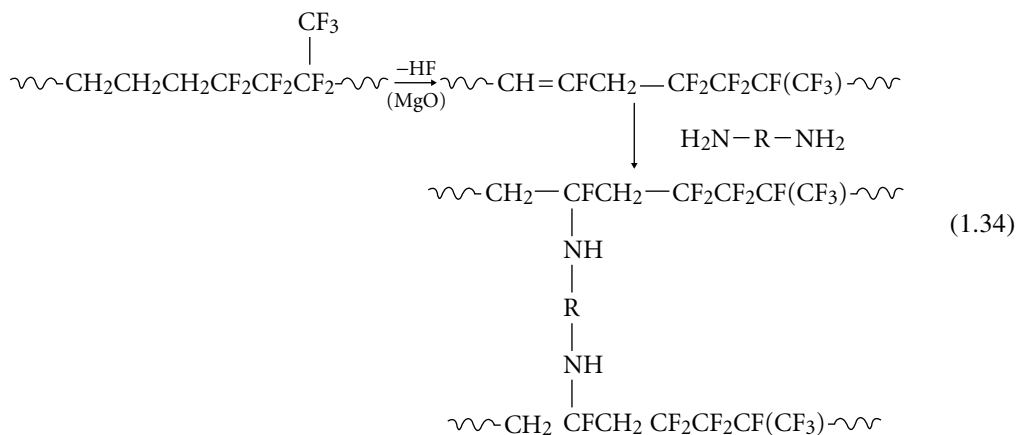


FIGURE 1.30 Equations for preparation of network glyptal resin.

Peroxide cross-linking of diene polymers works with all except butyl rubber, which undergoes chain scission. The cross-links formed via peroxides are more thermally stable than those formed via sulfur vulcanization. However, peroxide cross-linking is not economically competitive with sulfur cross-linking because of the high cost of peroxides. Peroxide cross-linking is primarily used for those polymers that cannot be easily cross-linked by sulfur, such as polyethylene and other polyolefins, ethylenepropylene (no diene) rubbers (EPM), and polysiloxanes. Cross-linking of polyethylene increases its strength properties and the upper limit of use temperature. Uses include electrical wire and cable insulation, pipe, and hose. For EPM and polysiloxanes, cross-linking is essential to their use as elastomers.

Cross-linking with elemental sulfur is the oldest method of vulcanization, discovered independently in 1839 by Goodyear in the United States and MacIntosh and Hancock in Great Britain. This results in many reactions, producing a variety of cross-links, as represented schematically in Figure 1.31. The rate of vulcanization with sulfur can be, and normally is, increased by addition of accelerators such as zinc salts of dithiocarbamic acids or organosulfur compounds such as tetramethylthiuram disulfide (see Chapter 2, Table 1.4). Other compounds, usually zinc oxide and stearic acid, are also added as activators. Although the mechanism of acceleration is not well understood, acceleration is known to increase the number of monosulfide and disulfide cross-links, and decrease the number of cyclic monosulfide groups (Figure 1.31).

Other cross-linking reactions are also used for elastomers. A variety of halogen-containing elastomers are cross-linked by heating with a basic oxide (e.g., MgO or ZnO) and a primary diamine. Such elastomers include poly(epichlorohydrin); various co-ad terpolymers of fluorinated monomers such as vinylidene fluoride, hexafluoropropylene, perfluoro(methyl vinyl ether), and tetrafluoroethylene (see “Fluoroelastomers”); and terpolymers of alkyl acrylate, acrylonitrile, and 2-chloroethyl vinyl ether (see “Polyacrylates”). Cross-linking involves dehydrohalogenation followed by addition of the diamine to the double bond (Equation 1.34) with the metal oxide acting as an acid acceptor. Some vulcanizations employ a dithiol instead of a diamine. Elastomeric terpolymers of alkyl acrylate, ethylene, and a small amount of alkenoic acid (see “Acrylate Polymers”) are vulcanized by addition of diamine. The alkenoic acid is added to introduce sites (C=C) for subsequent cross-linking via reaction with primary diamines.



The vulcanization of polychloroprene (Neoprene) is carried out in different ways. Conventional sulfur vulcanization is not practiced to a large extent, since best physical properties of neoprene rubber are achieved by vulcanization with metal oxides (without diamine), either alone or in combination with sulfur (sometimes together with an accelerator). Halogenated butyl rubber is cross-linked in a similar manner. The mechanism for cross-linking with metal oxide alone is not established.

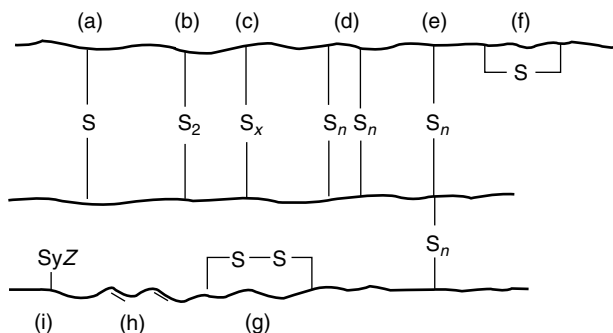


FIGURE 1.31 Typical chemical groupings in a sulfur-vulcanized natural rubber network. (a) Monosulfide cross-link; (b) disulfide cross-link; (c) polysulfide cross-link ($x=3-6$); (d) parallel vicinal cross-links ($n=1-6$) attached to adjacent main-chain atoms; (e) cross-links attached to common or adjacent carbon atoms; (f) intrachain cyclic monosulfide; (g) intrachain cyclic disulfide; (h) conjugated diene; (i) pendant sulfide group terminated by moiety Z derived from accelerator.

Aging of polymers is often accompanied by cross-linking due to the effect of the surroundings. Such cross-linking is undesirable because it greatly reduces the elasticity of the polymer, making it more brittle and hard. The well-known phenomenon of aging of polyethylene with loss of flexibility is due to cross-linking by oxygen under the catalytic action of sunlight (Figure 1.32a). Cheap rubber undergoes a similar loss of flexibility with time due to oxidative cross-linking (Figure 1.32b). This action may be discouraged by adding to the polymer an antioxidant, such as a phenolic compound and an opaque filler, such as carbon black, to prevent entry of light.

1.11.3 Radiation Cross-Linking

When vinyl polymers are subjected to ionizing radiation (whether it be photons, electrons, neutrons, or protons), two main types of reaction occur: cross-linking and degradation. Generally, both occur simultaneously, though degradation predominates with high doses of radiation. With low radiation doses, the polymer structure determines which will be the major reaction. Thus, geminally disubstituted polymers, such as poly(α -methylstyrene), poly(methylmethacrylate), and polyisobutylene tend to undergo chain scission, with monomer being formed as the major degradation product. Such polymers

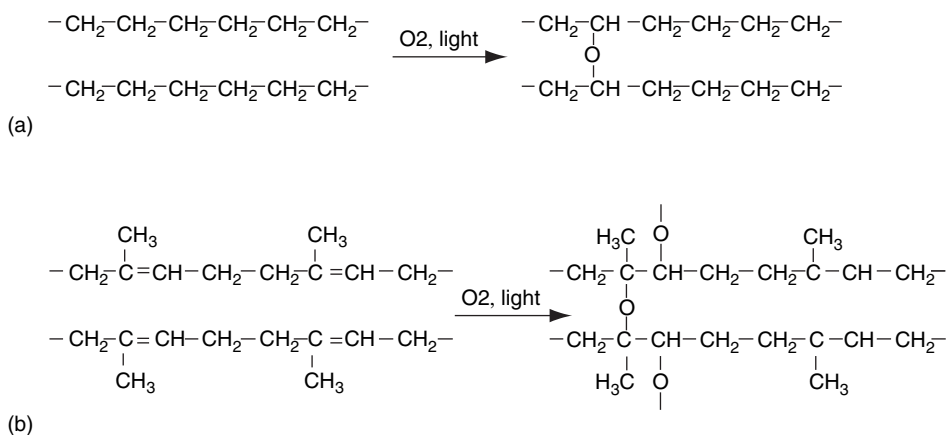


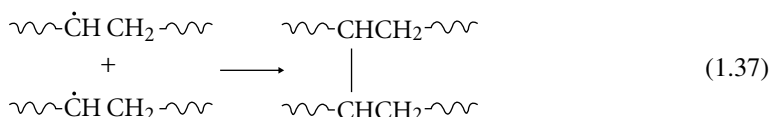
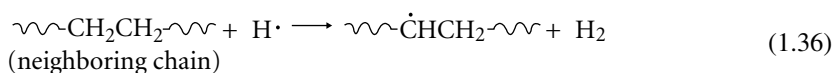
FIGURE 1.32 Aging of (a) polyethylene and (b) natural rubber by oxidative cross-linking.

TABLE 1.6 Behavior of Polymers Subjected to High Energy Radiation

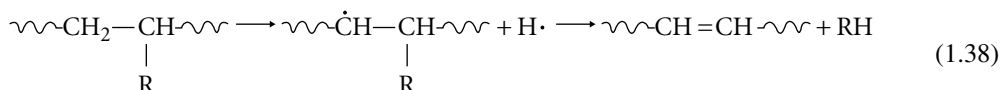
Polymers that Cross-Link	Polymers that Degrade
Polyethylene	Polyisobutylene
Poly(acrylic acid)	Poly(α -methyl styrene)
Poly(methyl acrylate)	Poly(methyl methacrylate)
Polyacrylamide	Poly(methacrylic acid)
Polychloroprene	Poly(vinylidene chloride)
Polydimethylsiloxanes	Polypropylene
Styrene-acrylonitrile copolymers	Polytetrafluoroethylene

will decrease in molecular weight on exposure to radiation. Halogen-substituted polymers, such as poly(vinyl chloride), degrade with loss of halogen. With most other vinyl monomers, cross-linking predominates. Table 1.6 lists some polymers that cross-link and some that degrade (i.e., liable to chain scission).

The mechanism of cross-linking is free-radical in nature. The reaction is essentially the same as in peroxide cross-linking except that polymer radicals are formed by the interaction of ionizing radiation with polymer. The reaction probably involves initial rejection of a proton (Equation 1.35), which in turn removes another proton from an adjacent site on a neighboring chain Equation 1.36. Cross-linking then occurs by radical combination as by Equation 1.37. This assumption is reasonable because hydrogen is a major side product, and random formation of radicals would not give the efficiency of cross-linking that is generally observed.



Low-density polyethylene gives rise to significant amounts of gaseous hydrocarbons on irradiation. This probably involves the ejection of a chain branch following the ejection of a proton (Equation 1.38).



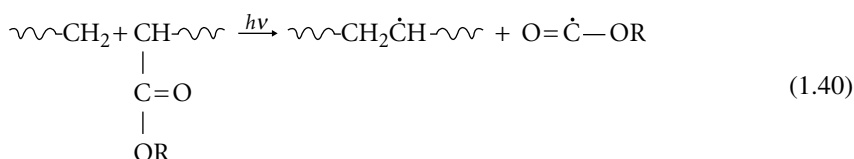
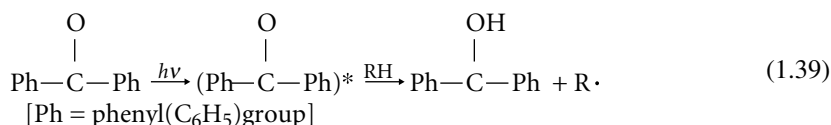
Fragmentation reactions of this type, as well as ejection of hydrogen, lead to double bonds in the polymer chains (Equation 1.38) in addition to cross-linking. Radiolysis effects on numerous vinyl polymers have been studied, but polyethylene is most important. Irradiated polyethylene film is used commercially because of its improved mechanical and thermal properties. Uses of radiation cross-linking include electrical wire and cable insulation and heat-shrinkable products (tubing, packaging film, and bags). Curing of coating and adhesives are other applications of radiation cross-linking. Polystyrene is quite resistant to radiation (a characteristic of aromatic polymers, in general), but it can be cross-linked with higher doses. A limitation of radiation cross-linking is that radiation does not penetrate deep into the polymer matrix. The method is therefore used primarily with films.

1.11.4 Photochemical Cross-Linking

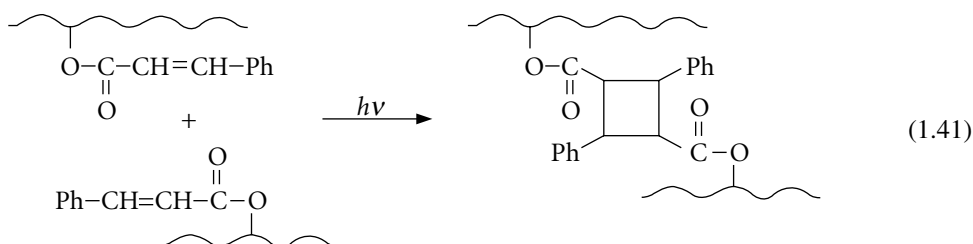
Ultraviolet or visible light induced cross-linking (photocross-linking) has assumed increasing importance in recent years. Among the numerous applications are printed circuits for electronic equipment; printing inks; coatings for optical fibers; varnishes for paper and carton board; and finishes for vinyl flooring, wood, paper, and metal. Photocross-linking applied to photoresist technology is described in Chapter 5.

There are two basic methods for bringing about photocross-linking of polymers; (1) incorporating photosensitizers which absorb photons and thereby induce formation of free radicals, and (2) incorporating groups into the polymer that undergo either light-initiated cross-linking polymerization or *photocycloaddition* reactions.

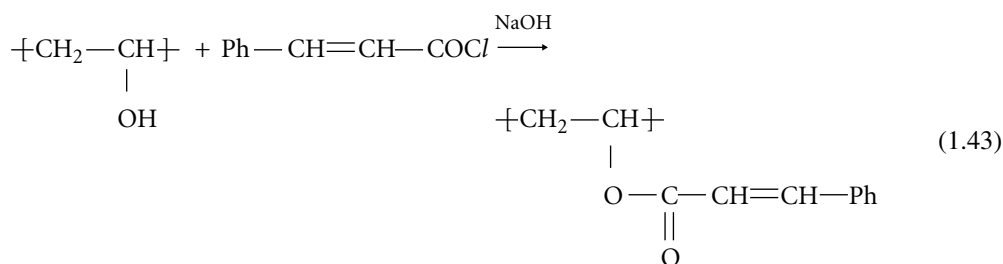
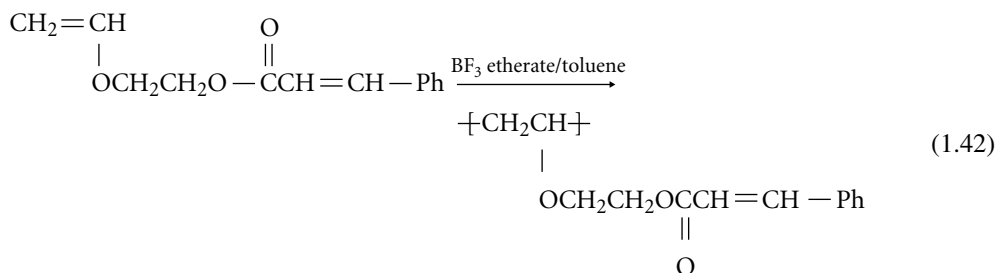
When photosensitizers such as benzophenone are added to polymer, absorption of ultraviolet radiation results in excitation of the sensitizer followed by hydrogen abstraction from the polymer to yield radical sites (Equation 1.39) available for cross-linking by combination reactions. Copolymers of vinyl esters and fluorinated monomers that can be cross-linked by ultraviolet radiation have been developed for use as weather-resistant wood coatings. In this application, the vinyl ester constitutes about 10% of the copolymer and benzophenone is added as a photosensitizer. The vinyl ester polymer also undergoes α -cleavage reaction (Equation 1.40) with subsequent cross-linking.



A wide variety of functional groups has been used to effect photocycloaddition or light-induced cross-linking. Among such groups are cinnamate (PhCH=CHCO₂R), chalcone (PhCH=CHCOPh), and stilbene (PhCH=CHPh). The groups may be present as part of the backbone or, more commonly, as pendant groups. In most cases, cycloaddition occurs to give cyclobutane cross-links, as shown for cinnamate ester in Equation 1.41.

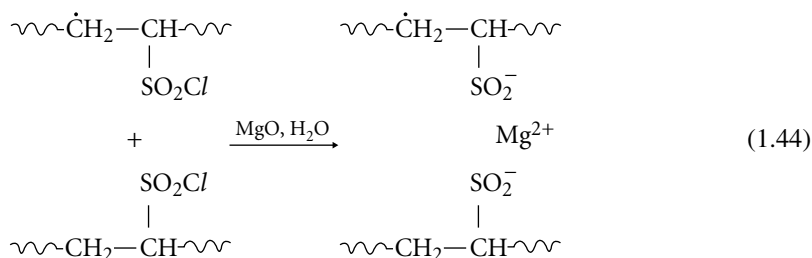


The reactive groups may be incorporated into polymer during the polymerization reaction; for example, β -vinylloxethyl cinnamate undergoes cationic polymerization through the vinyl ether (Equation 1.42) to yield a linear polymer containing pendant cinnamate ester. Alternatively, the group may be added to preformed polymer, as in the Schotten-Baumann reaction of poly(vinyl alcohol) with cinnamoyl chloride (Equation 1.43).



1.11.5 Ionic Cross-Linking

Ionic cross-links fall in the category of thermally labile cross-links, that is, chemical cross-links that break apart on heating and reform on cooling. Examples of ionic cross-linking are the hydrolysis of chlorosulfonated polyethylene with a divalent metal oxide and a source of water, and the neutralization of poly(ethylene-*co*-methacrylic acid) to salts of divalent metals. In a typical commercial product of chlorosulfonated polyethylene there is one chlorosulfonyl group for each 200 backbone carbon atoms. Magnesia (MgO) and a hydrogenated wood resin (as a source of H₂O) can be used as a cross-linking system to yield magnesium sulfonate cross-links in the polymer (Equation 1.44).



Neutralization of ethylene copolymers containing up to 5%–10% acrylic or methacrylic acid copolymer with a metal salt such as the acetate or oxide of zinc, magnesium, and barium yields products referred to as ionomers. (Commercial products may contain univalent as well as divalent metal salts.) Ionomers are marked by Du Pont under the trade name Surlyn. These have interesting properties compared with the nonionized copolymer. Introduction of ions causes disordering of the semicrystalline structure, which makes the polymer transparent. Ionomers act like reversibly cross-linked thermoplastics as a result of microphase separation between ionic metal carboxylate and nonpolar hydrocarbon segments. The

behavior is similar to the physical cross-linking in thermoplastic elastomers (see [Chapter 4](#)). Ionomers are discussed more fully in [Chapter 5](#).

1.12 Solubility Behavior of Polymers

Knowledge of the solubility of various polymers in different solvents is important in assessing their chemical resistance and their application potentialities in the fields of paints, spinning fibers, and casting films. Important also is the knowledge of the solubility of various materials, such as plasticizers and extenders in the polymer, especially since this has an important bearing on plastics formulation.

Because of the size and shape of the polymer molecules and other factors, the solubility relations in polymer systems are complex in comparison to those among low-molecular-weight compounds. Some empirical solubility rules have, nevertheless, been derived for applying to polymer systems, and it is also possible to make certain predictions about solubility characteristics of such systems.

The underlying reason that one material can act as a solvent for another is the compatibility of the materials—i.e., the ability of the molecules of the two materials to coexist without tending to separate. If we denote the force of attraction between the molecules of one material A by F_{AA} , that between the molecules of another material B by F_{BB} , and represent that between one A and one B molecule as F_{AB} , then the system will be compatible and a solution will result if $F_{AB} > F_{BB}$ and $F_{AB} > F_{AA}$. On the other hand, if F_{AA} or $F_{BB} > F_{AB}$, the system will be incompatible and the molecules will separate, forming two phases. In the absence of any specific interaction (e.g., hydrogen bonding) between solvent and solute, we can reasonably assume the intermolecular attraction forces between the dissimilar molecules to be approximately given by the geometric mean of the attraction forces of the corresponding pairs of similar molecules; that is, $F_{AB} = (F_{AA}F_{BB})^{1/2}$. Consequently, if F_{AA} and equal, F_{AB} will also be similar and the materials should be soluble.

1.12.1 Solubility Parameter

A measure of the intermolecular attraction forces in a material is provided by the cohesive energy. Approximately, this equals the heat of vaporization (for liquids) or sublimation (for solids) per mol. The cohesive energy density in the liquid state is thus $(\Delta E_v/V)$, in which ΔE_v is the molar energy of vaporization and V is the molar volume of the liquid. The square root of this cohesive energy density is known as the solubility parameter (δ), that is,

$$\delta = (\Delta E_v/V)^{1/2} \quad (1.45)$$

If the vapor behaves approximately like an ideal gas, Equation 1.45 can be written as

$$\delta = [(\Delta H_v - RT)/V]^{1/2} = [(\Delta H_v - RT)\rho/M]^{1/2} \quad (1.46)$$

where ΔH_v is the molar enthalpy of vaporization and ρ is the density of liquid with molecular weight M . For a volatile liquid cohesive energy density and, hence δ , can be determined experimentally by measuring ΔH_v and ρ .

Example 5

Calculate an estimate of the solubility parameter for water at 25°C from its heat of vaporization at the same temperature, given by



Answer. From Equation 1.46:

$$\begin{aligned}\delta^2 &= [(10,514 \text{ cal mol}^{-1}) - (1.987 \text{ cal mol}^{-1} \text{ K}^{-1})(298 \text{ K})](1 \text{ g cm}^{-3})/(18 \text{ g mol}^{-1}) \\ &= 551.2 \text{ cal cm}^{-3} = 2.3 \times 10^9 \text{ J m}^{-3}\end{aligned}$$

$$\delta = 23.5 \text{ (cal cm}^{-3})^{1/2} = 48.0 \times 10^3 \text{ (J m}^{-3})^{1/2} = 48 \text{ MPa}^{1/2}$$

[Conversion factors: $1 \text{ cal cm}^{-3} = 4.184 \times 10^6 \text{ m}^{-3} = 4.184 \times 10^6 \text{ Pa} = 4.184 \text{ MPa}$. Hence, $1 \text{ (cal cm}^{-3})^{1/2} = 2.045 \text{ MPa}^{1/2}$]

Hildebrand [21] first used the solubility parameter approach for calculating estimates of the enthalpy of mixing, ΔH_{mix} , for mixtures of liquids. The equation employed is

$$\Delta H_{\text{mix}} = V_{\text{mix}} \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad (1.47)$$

where V_{mix} is the molar volume of the mixture, and δ_1 and δ_2 are the solubility parameters of components 1 and 2, respectively.

A necessary requirement for solution and blending compatibility is a negative or zero Gibbs free energy change (ΔG_{mix}) when the solution or blend components are mixed, that is,

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \leq 0 \quad (1.48)$$

Since the ideal entropy of mixing (ΔS_{mix}) is always positive, the components of a mixture can be assumed to be miscible only if $\Delta H_{\text{mix}} \leq T \Delta S_{\text{mix}}$. Solubility therefore depends on the existence of a zero or small value of ΔH_{mix} , only positive (endothermic) heats of mixing being allowed, as in Equation 1.47. Miscibility or solubility will then be predicted if the absolute value of the $(\delta_1 - \delta_2)$ difference is zero or small [22]. Specific effects such as hydrogen bonding and charge transfer interactions can lead to negative ΔH_{mix} but these are not taken into account by Equation 1.47, and separate considerations must be applied in order to predict their effect on miscibility and solubility [23].

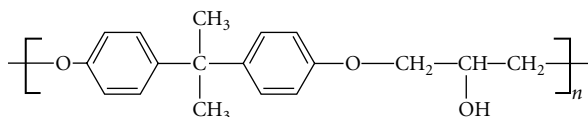
Solubility parameters of solvents can be correlated with the density, molecular weight, and structure of the solvent molecule. According to the additive method of Small [24], the solubility parameter is calculated from a set of additive constants, F , called molar attraction constants, by the relationship

$$\delta = \frac{\rho}{M} \sum F \quad (1.49)$$

where $\sum F$ is the molar attraction constants summed over the groups present in the compound; ρ and M are the density and the molar mass of the compound. The same procedure is applied to polymers and Equation 1.49 is used, wherein ρ is now the density of the amorphous polymer at the solution temperature, $\sum F_i$ is the sum of all the molar attraction constants for the repeat unit, and M is the molar mass of the repeat unit. Values of molar attraction constants for the most common groups in organic molecules were estimated by Small [24] from the vapor pressure and heat of vaporization data for a number of simple molecules. A modified version of a compilation of molar attraction constants [25,26] is reproduced in Table 1.7. An example of the use of the tabulated molar attraction constants is given in the problem worked out below.

Example 6

Calculate an estimate of the solubility parameter for the epoxy resin DGEBA (diglycidyl ether of bisphenol A) having the repeat unit structure as shown below and density 1.15 g/cm^3 .



Answer. M (for repeating unit) = 284 g/mol.

Groups	ΣF (cal cm ³) ^{1/2} /mol		
–CH ₃	147.3	2	294.60
–CH ₂	131.5	2	263.00
>CH–	85.99	1	85.99
>C<	32.03	1	32.03
–O– (ether)	114.98	2	229.96
–OH	225.84	1	225.84
–CH=(aromatic)	117.12	8	936.96
–C=(aromatic)	98.12	4	392.48
6-membered ring	–23.44	2	–46.88
Para substitution	40.33	2	80.66
$\delta = \frac{(1.15 \text{ g cm}^{-3})(2496.64 \text{ cal}^{1/2} \text{ cm}^{3/2} \text{ mol}^{-1})}{(284 \text{ g mol}^{-1})}$			2494.64
$= 10.1(\text{cal cm}^{-3})^{1/2} = 20.7 \text{ MPa}^{1/2}$			

The units of the solubility parameter δ are in (energy/volume)^{1/2}. The (δ values for some common solvents and polymers [27], listed in Table 1.8 and Table 1.9, have units of cal^{1/2} cm^{3/2}, called hildebrands. The SI value in MPa^{1/2} may be obtained by multiplying the δ value in hildebrand by 2.045. Most tabulated solubility parameters refer to 25°C. However, over the temperature range normally encountered in industrial practice, the temperature dependence of δ can be neglected.

While the solubility parameter of a homopolymer can be calculated from the molar attraction constants as illustrated in Example 6, the solubility parameter of random copolymers, δ_c , may be calculated from

$$\delta_c = \sum \delta_i w_i \quad (1.50)$$

where δ_i is the solubility parameter of the homopolymer that corresponds to the monomer i in the copolymer and w_i is the weight fraction of repeating unit i in the copolymer [28].

Solubility would be expected if the absolute value of ($\delta_1 - \delta_2$) is less than about unity and there are no strong polar or hydrogen-bonding interactions in either the polymer or the solvent. To allow for the influence of hydrogen-bonding interactions, solvents have been characterized qualitatively as poorly, moderately, or strongly hydrogen bonded. The solvents listed in Table 1.8 are grouped according to this scheme. It is a useful practice to match both solubility parameter and hydrogen-bonding tendency for predicting mutual solubility.

Hansen [29] developed a three-dimensional solubility parameter system based on the assumption that the energy of evaporation, i.e., the total cohesive energy ΔE_t which holds a liquid together, can be divided into contribution from dispersion (London) forces ΔE_d , polar forces ΔE_p , and hydrogen-bonding forces ΔE_h . Thus,

$$\Delta E_t = \Delta E_d + \Delta E_p + \Delta E_h \quad (1.51)$$

TABLE 1.7 Group Molar Attraction Constants

Group	Molar Attraction, F (cal cm ³) ^{1/2} mol ⁻¹
-CH ₃	147.3
-CH ₂ -	131.5
>CH-	85.99
>C<	32.03
CH ₂ =(olefin)	126.54
-CH=(olefin)	121.53
>C=(olefin)	84.51
-CH=(aromatic)	117.12
-C=(aromatic)	98.12
-O-(ether, acetal)	114.98
-O-(epoxide)	176.20
-COO-	326.58
>C=O	262.96
-CHO	292.64
(CO) ₂ O	567.29
-OH-	225.84
-OH aromatic	170.99
-NH ₂	226.56
-NH-	180.03
-N-	61.08
-C≡N	354.56
-N=C=O	358.66
-S-	209.42
Cl ₂	342.67
-Cl (primary)	205.06
-Cl (secondary)	208.27
-Cl (aromatic)	161.0
-Br	257.88
-Br (aromatic)	205.60
-F	41.33
Structure Feature	
Conjugation	23.26
Cis	-7.13
Trans	-13.50
5-membered ring	20.99
6-membered ring	-23.44
Ortho substitution	9.69
Meta substitution	6.6
Para substitution	40.33

Source: Hoy, K. L. 1970. *J. Paint Technol.*, 42, 76 and Brandrup J. and Immergut E. eds., 1975. *Polymer Handbook*, 2nd Ed. Wiley Interscience, New York.

Dividing this equation by the molar volume of a solvent, V , gives

$$\frac{\Delta E_t}{V} = \frac{\Delta E_d}{V} + \frac{\Delta E_p}{V} + \frac{\Delta E_h}{V} \quad (1.52)$$

or

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1.53)$$

where δ_d , δ_p , and δ_h are solubility parameters due to dispersion forces, dipole forces, and hydrogen-bonding (or, in general, due to donor-acceptor interactions), respectively. The three parameters, called Hansen parameters, were determined [29,30] empirically on the basis of many experimental observations

TABLE 1.8 Solubility Parameters for Some Common Solvents

Solvent	δ (cal/cm ³) ^{1/2}
(i) Poorly H-bonded (Hydrocarbons and their halo-, nitro-, and cyano-Products)	
<i>n</i> -Hexane	7.3
Carbon tetrachloride	8.6
Toluene	8.9
Benzene	9.2
Chloroform	9.3
Methylene chloride	9.7
Nitrobenzene	10.0
Acetonitrile	11.9
(ii) Moderately H-bonded (esters, ethers, ketones)	
Isoamyl acetate	7.8
Dioctyl phthalate	7.9
Tetrahydrofuran	9.1
Methyl ethyl ketone	9.3
Acetone	9.9
1,4-Dioxane	10.0
Diethylene glycol	
Monoethyl ether	10.2
(iii) Strongly hydrogen-bonded (acids, alcohols, aldehydes, amides, amines)	
Piperidine	8.7
Acetic acid	10.1
Meta-cresol	10.2
<i>t</i> -Butanol	10.6
<i>I</i> -Butanol	11.4
Propylene glycol	12.6
Methanol	14.5
Ethylene glycol	14.6
Glycerol	16.5
Water	23.4

Source: Brandrup, J. and Immergut, E. eds. 1975. *Polymer Handbook*, 2nd Ed. Interscience, Wiley, New York.

SI value of δ in MPa^{1/2} is obtained by multiplying the value in (cal/cm³)^{1/2} by 2.045.

for a large number of solvents (Table 1.10). Hansen's total cohesion parameter, δ_t , corresponds to the Hildebrand parameter δ , although the two quantities may not be identical because they are determined by different methods. Once the three component parameters for each solvent were evaluated, the set of parameters could then be obtained for each polymer (Table 1.11) from solubility ascertained by visual inspection of polymer–solvent mixtures (at concentrations of 10% w/v).

When plotted in three dimensions, the Hansen parameters provide an approximately spherical volume of solubility for each polymer in δ_d , δ_p , δ_h space. The scale on the dispersion axis is usually doubled to improve the spherical nature of this volume. The distance of the coordinates ($\delta_d^i, \delta_p^i, \delta_h^i$) of any solvent i from the center point ($\delta_d^j, \delta_p^j, \delta_h^j$) of the solubility sphere of polymer j is

$$d = [4(\delta_d^i - \delta_d^j)^2 + (\delta_p^i - \delta_p^j)^2 + (\delta_h^i - \delta_h^j)^2]^{1/2} \quad (1.54)$$

This distance can be compared with the radius R of the solubility sphere [31] of the polymer (Table 1.11), and if $d < R$, the likelihood of the solvent i dissolving the polymer j is high. This works well, despite the limited theoretical justification of the method.

Example 7

Using Hansen parameters (Table 1.10 and Table 1.11) determine if polystyrene is expected to dissolve in a solvent mixture of 60/40 v/v methyl ethyl ketone/*n*-hexane.

TABLE 1.9 Solubility Parameters for Some Common Polymers

Polymer	δ , (cal/cm ³) ^{1/2}	H-Bonding Group ^a
Polytetrafluoroethylene	6.2	Poor
Polyethylene	8.0	Poor
Polypropylene	9.2	Poor
Polyisobutylene	8.0	Poor
Polybutadiene	8.4	Poor
Polyisoprene	8.1	Poor
Polystyrene	9.1	Poor
Poly(methyl methacrylate)	9.5	Medium
Poly(vinyl acetate)	9.4	Medium
Poly(vinyl chloride)	9.7	Medium
Cellulose diacetate	11.0	Strong
Poly(vinyl alcohol)	12.6	Strong
Polyacrylonitrile	12.7	Poor
Nylon-6,6	13.7	Strong

SI value of δ , in MPa^{1/2} is obtained by multiplying the value in (cal/cm³)^{1/2} by 1.045.

Source: Burrell, H. 1975. *Polymer Handbook*, J. Brandrup and E. Immergut, eds., 2nd Ed., pp. IV-337–359. Wiley Interscience, New York.

^a The hydrogen-bonding group of each polymer has been taken as equivalent to that of the parent monomer.

Answer. Denote the solubility parameter components of MEK, *n*-hexane, and polystyrene using superscripts *i*, *j*, and *k*, respectively. From Table 1.10:

$$\text{MEK: } \delta_d^i = 7.8, \quad \delta_p^i = 4.4, \quad \delta_h^i = 2.5 \text{ all in (cal cm}^{-3}\text{)}^{1/2}$$

TABLE 1.10 Hansen Parameters for Solvents at 25°C

Liquid	δ_d (cal/cm ³) ^{1/2}	δ_p (cal/cm ³) ^{1/2}	δ_h (cal/cm ³) ^{1/2}
Acetic acid	6.8	6.0	9.2
Acetone	6.3	4.8	5.4
Benzene	7.9	4.2	2.0
<i>I</i> -Butanol	7.8	2.8	7.7
Chloroform	5.4	6.7	3.1
Cyclohexane	8.0	1.5	0.0
1,4-Dioxane	8.0	4.9	3.9
Diethyl phthalate	8.1	3.4	1.5
Ethyl acetate	6.5	4.2	4.3
Ethylene glycol	4.9	7.4	14.6
Glycerol	4.5	7.5	15.3
<i>n</i> -Hexane	7.3	0.0	0.0
Methyl ethyl ketone	7.8	4.4	2.5
Methanol	7.4	6.0	10.9
Nitrobenzene	8.6	6.8	0.0
Tetrahydrofuran	8.2	2.8	3.9
Toluene	8.0	3.9	0.8
Water	5.9	11.1	19.7
<i>m</i> -Xylene	8.1	3.5	1.2

SI value of a parameter in MPa^{1/2} is obtained by multiplying the value in (cal/cm³)^{1/2} by 2.045.

Source: From “Tables of Solubility Parameters” 3rd Ed. Chemicals and Plastics Research and Development Dept., Union Carbide Corporation. Terrytown. N.Y., 1975.

TABLE 1.11 Hansen Parameters and Interactions Radius of Some Polymers and Resins

Polymer	δ_d (cal/cm ³) ^{1/2}	δ_p (cal/cm ³) ^{1/2}	δ_h (cal/cm ³) ^{1/2}	R (cal/cm ³) ^{1/2}
Acrylonitrile–butadiene elastomer	9.1	4.3	2.0	4.7
Cellulose acetate	9.1	6.2	5.4	3.7
Epoxy resin	10.0	5.9	5.6	6.2
Nitrocellulose	7.5	7.2	4.3	5.6
Polyamide, thermoplastic	8.5	−0.9	7.3	4.7
Polyisoprene	8.1	0.7	−0.4	4.7
Poly(methyl methacrylate)	9.1	5.1	3.7	4.2
Polystyrene	10.4	2.8	2.1	6.2
Poly(vinyl acetate)	10.2	5.5	4.7	6.7
Poly(vinyl chloride)	8.9	3.7	4.0	1.7
Styrene–butadiene rubber	8.6	1.7	1.3	3.2

SI value in MPa^{1/2} is obtained by multiplying the value in (cal/cm³)^{1/2} by 2.045.

Source: Data from Hansen, C. M. and Beerbower, A. 1971. *Kirk Othmer Encyclopaedia of Chemical Technology*, A. Standen, ed., 2nd Ed., Suppl. 889, p. 910. Wiley Interscience, New York.

$$n - \text{hexane: } \delta_d^j = 7.3, \quad \delta_p^j = 0, \quad \delta_h^j = 0 \text{ all in (cal cm}^{-3}\text{)}^{1/2}$$

The Hansen parameters are combined on a 60/40 volume fraction basis:

$$\delta_d^{ij} = 0.6 \times 7.8 + 0.4 \times 7.3 = 7.6 \text{ (cal cm}^{-3}\text{)}^{1/2}$$

$$\delta_p^{ij} = 0.6 \times 4.4 + 0.4 \times 0.0 = 2.6 \text{ (cal cm}^{-3}\text{)}^{1/2}$$

$$\delta_h^{ij} = 0.6 \times 2.5 + 0.4 \times 0.0 = 1.5 \text{ (cal cm}^{-3}\text{)}^{1/2}$$

For polystyrene (Table 1.11):

$$\delta_d^k = 10.4, \quad \delta_p^k = 2.8, \quad \delta_h^k = 2.1, \quad R = 6.2 \text{ all in (cal cm}^{-3}\text{)}^{1/2}$$

From Equation 1.54: $d = [4(10.4 - 7.6)^2 + (2.8 - 2.6)^2 + (2.1 - 1.5)^2]^{1/2} = 5.6 \text{ (cal cm}^{-3}\text{)}^{1/2}$ As this value is less than the radius of the polymer solubility sphere ($6.2 \text{ cal}^{1/2} \text{ cm}^{-3/2}$), the polymer is expected to be soluble. This is found to be the case for a 10% w/w solution.

Three-dimensional presentations of solubility parameters are not easy to use and it is more convenient to transform the Hansen parameters into fractional parameters as defined by [32]:

$$\begin{aligned} f_d &= \delta_d / (\delta_d + \delta_p + \delta_h) \\ f_p &= \delta_p / (\delta_d + \delta_p + \delta_h) \\ f_h &= \delta_h / (\delta_d + \delta_p + \delta_h) \end{aligned} \quad (1.55)$$

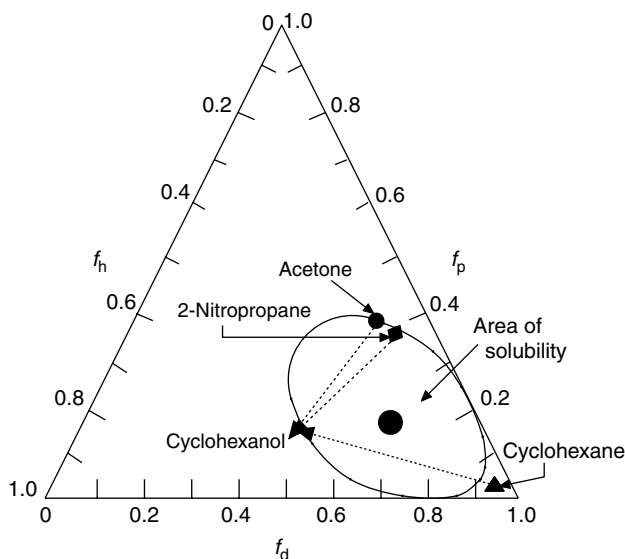


FIGURE 1.33 Limiting solubility boundary for chlorinated rubber. The solid circle represents the probable solubility parameter of the resin. (After Teas, J. P. 1968. *J. Paint Technol.*, 40, 519.)

The fractional parameters represent, in effect, the quantitative contribution of the three types of forces to the dissolving abilities for each solvent and can be represented more conveniently in a triangular diagram (Figure 1.33) to provide a visual presentation of the nature of the solvating powers of liquids, including in one picture such diverse liquids as water, alcohols, organic acids, and hydrocarbons [32]. The triangular solubility chart can be used conveniently for the prediction of solubility of polymers. A chart can be constructed for a given resin, identifying each solvent coordinate point to indicate either complete, partial or lack of solubility. In general, solvents which provide clear solutions are grouped in a reasonably well defined area of the chart thus forming a loop and solvents which tend to swell the resin lie near the border of such loops, as shown in Figure 1.33. The probable solubility parameters of the solute polymer will be at the heart of the solubility area. Any solvent possessing values of f_d , f_p , and f_h to place its plot inside the solubility area has a high probability of producing a clear solution. Conversely, liquids lying outside of the solubility area are very likely to be poor or nonsolvent.

Since δ_d values do not vary greatly, at least among common solvents, it has been suggested that a plot of δ_p versus δ_h should be sufficient for most practical purposes. Thus, another and probably more efficient two-parameter representation is made possible by defining [33]

$$\delta_v \equiv (\delta_d^2 + \delta_p^2)^{1/2} \quad (1.56)$$

The procedures outlined above have a practical use, but it should be realized that the parametric models are almost entirely empirical. Experimental uncertainties are also involved since solubility measurements are not very accurate. Solubility loops described by the models only indicate the limits of compatibility and always include doubtful observations.

1.13 Effects of Corrosives on Polymers

Polymers are resistant to electrochemical corrosion. When a polymer has a δ value similar to that of water, dissolution occurs. However, if the δ value of the polymer is lower, it is not attacked by water or other polar solvents. The carbon-carbon bonds in polymer backbones are not cleaved even by boiling water. When amide, ester, or urethane groups are present in the polymer backbone, they may be attacked

TABLE 1.12 Effects of Corrosive Environments on Plastics

Plastic	Environment															
	Aliphatic Solvents		Aromatic Solvents		Chlorinated Solvents		Esters and Ketones		Weak Bases		Strong Bases		Strong Acids		Strong Oxidants	
Acetal	A	B	A	B	A	B	A	B	A	A	A	B	E	E	E	E
Acrylic	B	C	E	E	E	E	E	E	A	C	B	E	D	E	E	E
Acrylonitrile–butadiene–styrene (ABS)	A	E	D	E	E	E	E	E	A	C	A	C	B	E	D	E
Cellulose acetate	A	B	A	C	A	D	E	E	A	C	C	E	C	E	C	E
Cellulose acetate butyrate	A	C	D	E	D	E	E	E	B	D	C	E	C	E	C	E
Cellulose acetate propionate	A	C	D	E	D	E	E	E	A	B	C	E	C	E	C	E
Epoxy (glass fiber filled)	A	B	A	B	A	C	B	C	A	A	B	C	B	C	D	D
Furan (asbestos filled)	A	A	A	A	A	A	A	A	B	B	B	B	A	A	E	E
Melamine	A	A	A	A	A	A	A	B	B	C	B	C	B	C	B	C
Phenolic (asbestos filled)	A	A	A	A	A	A	C	C	A	C	D	E	A	A	D	E
Polyamide	A	A	A	A	A	B	A	A	A	B	B	C	E	E	E	E
Polybenzimidazole	A	A	A	A	A	A	A	A	A	A	A	B	A	B	A	C
Polycarbonate	A	A	A	A	E	E	E	E	A	E	E	E	A	A	A	A
Poly(chlorotrifluoroethylene)	A	A	A	A	C	D	A	A	A	A	A	A	A	A	A	A
Polyester (glass fiber filled)	A	B	A	C	B	D	C	C	B	C	C	E	B	B	B	C
Polyethylene	C	E	C	E	D	E	D	E	A	A	A	A	A	A	A	A
Polypropylene	A	D	B	D	B	D	A	C	A	A	A	A	A	C	A	D
Polysulfone	A	A	D	D	E	E	C	D	A	A	A	A	A	A	A	A

(continued)

TABLE 1.12 (Continued)

Plastic	Environment															
	Aliphatic Solvents		Aromatic Solvents		Chlorinated Solvents		Esters and Ketones		Weak Bases		Strong Bases		Strong Acids		Strong Oxidants	
Polystyrene	D	E	D	E	E	E	D	E	A	E	A	E	D	E	D	E
Poly(tetrafluoroethylene)	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Polyurethane	A	D	C	D	D	E	B	C	A	A	C	D	A	D	A	D
Poly(vinyl chloride)	A	E	D	E	E	E	D	E	A	E	A	E	A	E	B	E
Silicone	B	C	D	D	D	E	B	D	A	B	D	E	C	D	D	E
Urea	A	C	A	C	A	C	A	B	B	C	B	C	D	E	B	C

Code: A=no effect or inert; B=slight effect; C=mild effect; D=softening or swelling; E=severe deterioration. The effects were measured at 25°C (first letter in each column) and at 90°C (second letter in each column).

by hot acids or alkalis, and hydrolysis may occur. When these functional groups are present as pendant groups on the polymer chain, the reaction will be similar. However, the tendency for such attack is reduced when alkyl groups are present on the carbon atom attached to the functional group. Thus, poly(methyl methacrylate) but not poly(methyl acrylate) is resistant to acid or alkaline hydrolysis. Atoms or groups with strong carbon bonds, such as fluorine, chlorine, and ether groups, are resistant to attack by aqueous acids and alkalis. The chemical resistance of various plastics is summarized in [Table 1.12](#).

1.14 Thermal Stability and Flame Retardation

Most organic polymers decompose when heated to moderate or high temperatures. It is for this reason that few synthetic polymers can be used for long periods of time above 150°C–200°C. This necessitates the use of metals and ceramics for many applications, even though synthetic polymers may be cheaper and, in some cases, stronger on a weight-for-weight basis.

Plastics can be grouped into eight temperature-time zones, depending on the temperature at which they retain 50% mechanical or physical properties when heated for different periods in air. These temperature–time zones are shown in Figure 1.34, and the materials falling in the different zones are listed in [Table 1.13](#). The materials in zone 6 and above can compete with metals in high-performance applications because they perform in the same temperature range. Most polymers in zone 6 and above do not burn, but they may char and may be consumed very slowly in direct flames.

Rotation of chain segments is more difficult in polymers with cyclic rings in their chains. As a result, such polymers are stiffer and more resistant to deformation and have higher melting points and higher

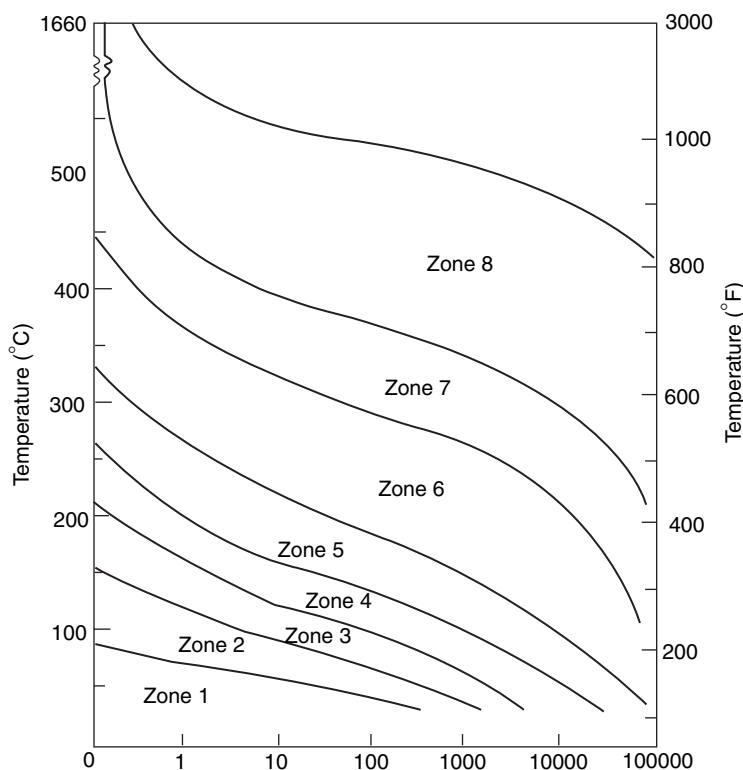


FIGURE 1.34 Time-temperature zones indicating thermal stability of plastics (see Table 1.13). (Adapted from Anon. 1968. *Plastics World*, 26(3), 30.)

TABLE 1.13 Plastics Retaining 50% Mechanical or Physical Properties at Temperature in Air*Zone 1*

Acrylic
 Cellulose acetate
 Cellulose acetate butyrate
 Cellulose acetate propionate
 Cellulose nitrate
 Polyallomer
 Polyethylene, low density
 Polystyrene
 Poly(vinyl acetate)
 Poly(vinyl alcohol)
 Poly(vinyl butyral)
 Poly(vinyl chloride)
 Styrene-acrylonitrile
 Styrene-butadiene
 Urea-formaldehyde

Zone 2

Acetal
 Acrylonitrile-butadiene-styrene Copolymer
 Ethyl cellulose
 Ethylene-vinyl acetate copolymer
 Furan
 Lonomer
 Polyamides
 Polycarbonate
 Polyethylene, high density
 Polyethylene, cross-linked
 Poly(ethylene terephthalate)
 Polypropylene
 Poly(vinylidene chloride)
 Polyurethane

Zone 3

Poly(monochlorotrifluoroethylene)

Zone 4

Alkyd
 Fluorinated ethylene propylene copolymer
 Melamine formaldehyde
 Phenol-furfural
 Polyphenylene oxide
 Polysulfone

Zone 5

Diallyl phthalate
 Epoxy
 Phenol-formaldehyde
 Polyester
 Poly(tetrafluoroethylene)

Zone 6

Polybenzimidazole
 Polyphenylene
 Silicone

Zone 7

Polyamide-imide
 Polyimide

Zone 8

High-performance plastics being developed using intrinsically rigid linear macromolecules rather than the conventional crystallization and cross-linking

Source: Anon. 1968. *Plastics World*, 26(3), 30.

glass transition temperatures. Thermal stability is improved by the presence of aromatic and heterocyclic rings in polymer chains. This general approach has resulted in a number of new commercially available polymers with improved high-temperature properties. Polyimides and polybenzimidazoles are important examples of such high-temperature polymers. They can be exposed for a short time to temperatures as high as 1,112°F (600°C).

Polyimides are synthesized [35] by the reactions of dianhydrides with diamines in a two-stage process (Figure 1.35). In the first stage, the two materials form an intermediate poly(amic acid). Processing is accomplished after this stage, since the polymer at this point is still soluble and fusible. The poly(amic acid) is formed into the desired physical form of the final polymer product (e.g., film, fiber, laminate, coating, etc.) and then the second stage of the reaction is carried out, in which the poly(amic acid) is cyclized in the solid state to the polyimide by heating at moderately high temperatures (above 150°C). The polymer after the second stage of the process is insoluble and infusible. Instead of *m*-phenylenediamine, shown in Figure 1.35, other diamines have also been used to synthesize polyimides—for example, *p*-phenylenediamine, *p,p'*-diaminodiphenyl ether, and *p,p'*-diaminodiphenyl sulfide.

Polyimides have been used up to 100 h at 600°F (315.6°C). They have been used as a transparent head cover for fire fighters and as excellent flame- and high-temperature-resistant foams, which can be used as structurally stable insulation materials at high temperatures. Polyimide/glass fiber composites have many uses in the electronics and aerospace industries and in other high-performance applications.

Polybenzimidazoles are synthesized by the reactions of aromatic diacids and aromatic tetraamines (Figure 1.36). Polybenzimidazoles are mostly used as fibers in parachutes, for reentry vehicles, and so on. Composites of polybenzimidazoles with fibers have excellent basic strength and high-temperature performance. These composites have been extensively used in nose fairings, aircraft leading edges, reentry nose cones, radomes, and deicer ducts.

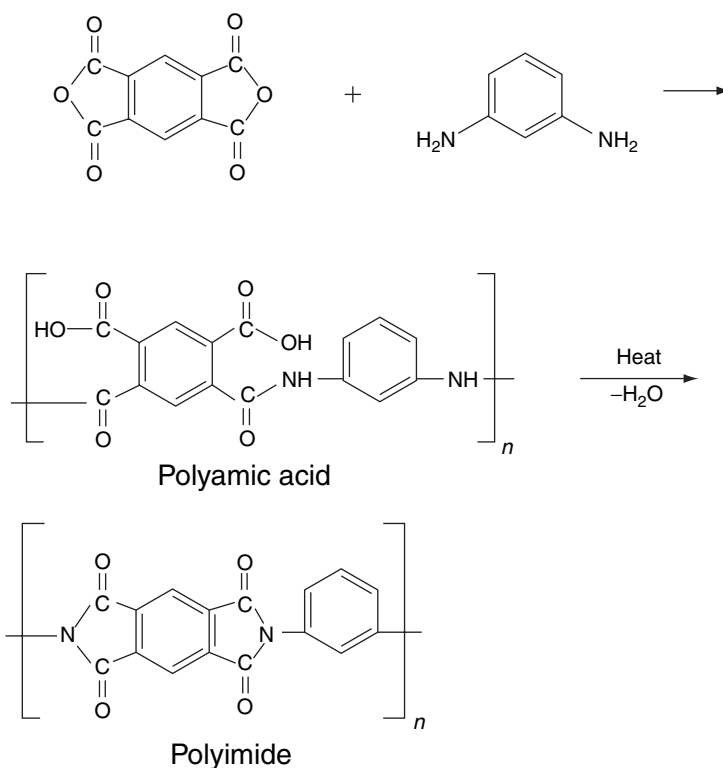


FIGURE 1.35 Synthesis of polyimide from pyromellitic anhydride and *m*-phenylenediamine.

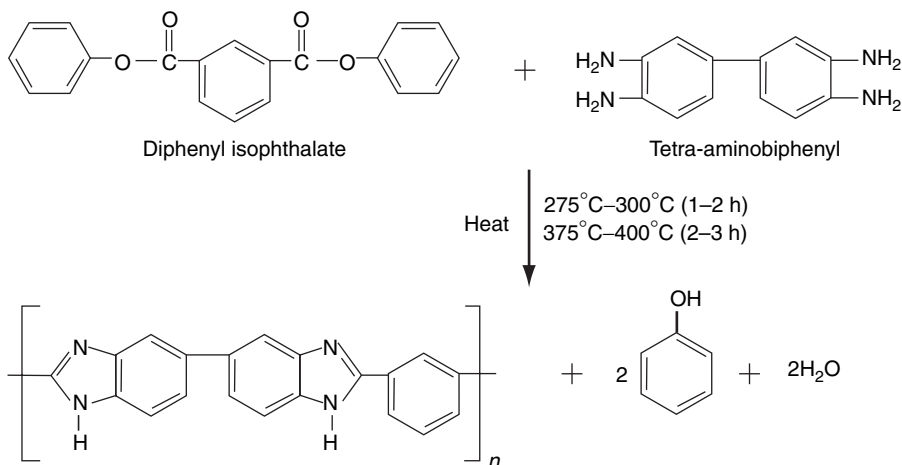


FIGURE 1.36 Synthesis of polybenzimidazole by condensation polymerization.

A weak link in the polybenzimidazole structure is the imino hydrogen. When this hydrogen is replaced by a phenyl group as in *N*-phenyl polybenzimidazole, a dramatic increase in high-temperature properties in oxidizing atmospheres is obtained.

In polymers such as polybiphenylenes there are a few aliphatic linkages and many aromatic rings which account for their improved heat resistance. Several polyphenylenes are shown in Figure 1.37. Poly(phenylene oxide) has excellent dimensional stability at elevated temperatures. Repeated steam autoclaving does not deteriorate its properties. Poly(phenylene sulfide) is completely nonflammable. It is used in the form of composites with both asbestos and glass fibers.

Aliphatic linkage is completely eliminated in ladder polymers such as polybenzimidazopyrrolones, commonly called “pyrrones” (Figure 1.38). Such polymers are highly stable in air. They do not burn or melt when heated but form carbon char without much weight loss. They are potentially the ultimate in heat- and flame-resistant materials.

Another way to get good heat resistance is to use inorganic material as backbone chain as in silicone polymers. Here organic radicals are attached to silicone atoms on an inorganic silicon–oxygen structure. Presence of silicon–oxygen links gives such materials outstanding heat resistance. A silicone polymer has the structure

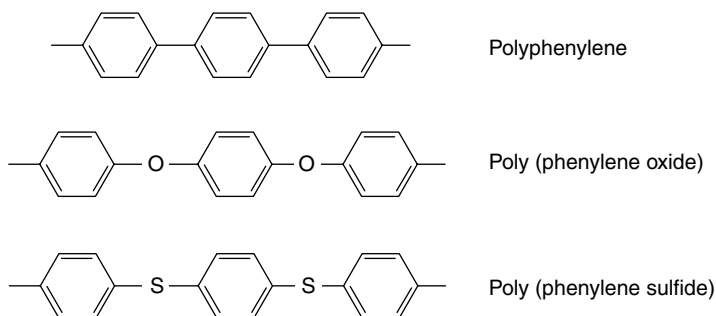


FIGURE 1.37 Structures of some polyphenylenes.

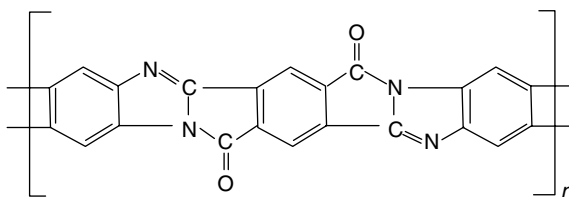
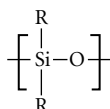


FIGURE 1.38 Typical structure of a polybenzimidazopyrrolone.

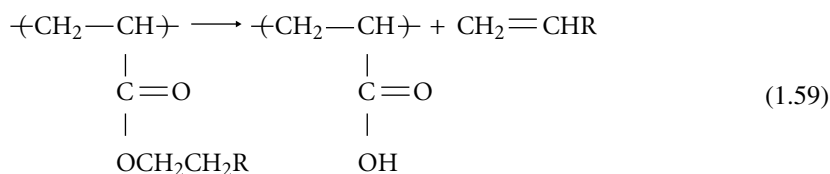
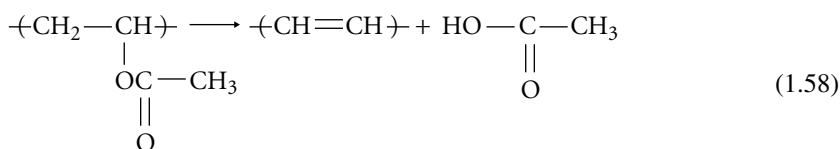
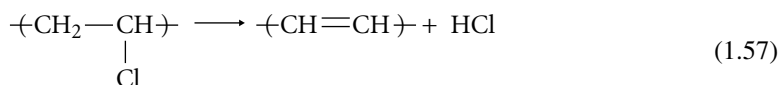


When n is a small number, the structure is that of a silicone oil, whereas silicon rubbers have high values of n . When the ratio R/Si is lower than 2, cross-linked polymers are obtained. Properties of silicone polymers are greatly affected by the type of organic radical present. For a given chain length, a methyl silicone can be an oily liquid, but a phenyl silicone is a hard and brittle resin.

1.14.1 Thermal Degradation

There are basically three types of thermal degradation reactions for vinyl polymers [36,37]: (1) nonchain scission; (2) random chain scission; and (2) depropagation. In practice, mechanisms 2 and 3 blend into one another, with many polymers showing evidence of both processes.

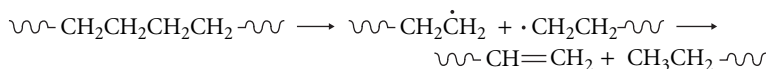
Nonchain scission refers to reactions involving pendant groups that do not break the backbone. Typical of such reactions are dehydrochlorination of poly(vinyl chloride) (Equation 1.57), elimination of acid from poly(vinyl esters)—for example, poly(vinyl acetate) (Equation 1.58)—and elimination of alkene from poly(alkyl acrylate)s (Equation 1.59).



The first two reactions lead to highly colored residues, indicating that the double bonds formed in the polymer backbone are primarily conjugated. Such elimination reactions are not satisfactory for synthesizing polyacetylene, however, since side reactions also occur. But nonchain scission has been

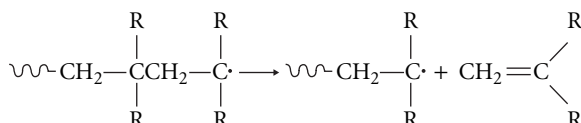
used as one approach to solving problem of polyacetylene's intractability (see "Inherently Conducting Polymers" in Chapter 5).

Random chain scission results from homolytic bond-cleavage reactions at weak points in the polymer chains. Complex mixtures of degradation products are formed, the origin of which may be explained in terms of radical transfer reactions such as



Random chain scission occurs with all vinyl polymers to varying degrees, but it occurs less with increasing substitution on the polymer backbone.

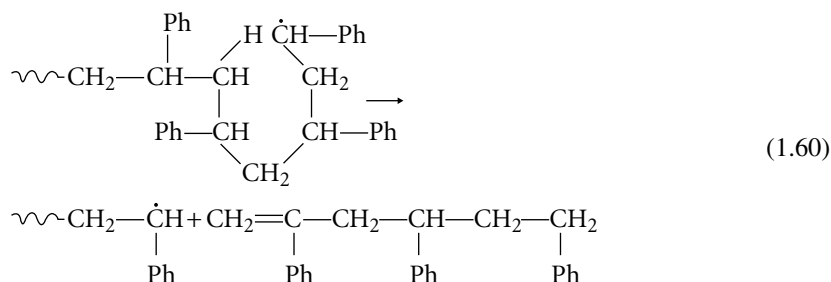
Depropagation, or depolymerization (unzipping), to give monomer occurs mainly with polymers prepared from 1,1-disubstituted monomers. The depolymerization is a free-radical process that may be initiated either at a chain end or at a random site on the backbone. For example, poly(methyl methyl methacrylate) appears to begin unzipping primarily at the chain ends, whereas poly(α -methylstyrene) does so at random sites along the chain. In both cases, tertiary radicals are formed with each depropagation step:



The nature of active chain ends in poly(methyl methacrylate) is a question for debate. At moderate temperatures (220°C) only half of the chains in this polymer unzip, and higher temperatures (350°C) may be needed to decompose the remaining polymer. Apparently, chains which unzip at 200°C are terminated by unsaturated groups, whereas those which depolymerize only at higher temperatures have saturated end groups.

Like poly(methyl methacrylate) and poly(α -methyl styrene), polytetrafluoroethylene also undergoes 100% conversion to the monomer at elevated temperatures. However, it does so only at low pressures and high temperatures. At atmospheric pressure, the monomer molecules recombine to form dimer and other species. This polymer is one of the most thermally stable polyolefins known, but even so, it cannot withstand prolonged exposure to temperatures above about 350°C–400°C.

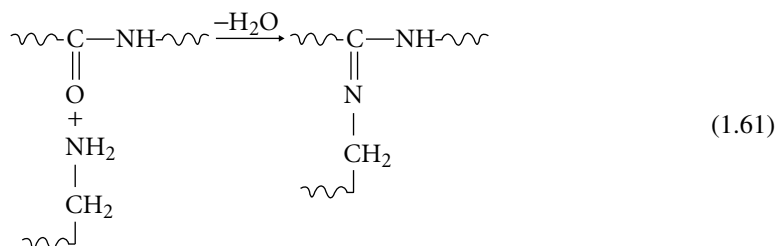
Polystyrene represents a case in which monomer is only one of several species formed by thermal degradation at 350°C as monomer, dimer, trimer, and tetramer are formed in the relative proportions of 40:10:8:1. The thermal breakdown process is believed to begin at unsaturated linkages which constitute the weak points along the chain. A cleavage at these sites initiates a free-radical mechanism leading to liberation of monomer and to an intramolecular back-biting process. The process liberates dimer, trimer, and so on, by a transfer mechanism such as the shown in Equation 1.60



Polyethylene yields very little monomer by thermal degradation. Above about 300°C, the

decomposition products form a continuous spectrum of unsaturated hydrocarbons which contain from 1 to at least 70 carbon atoms. The products are believed to be the results of random chain cleavage accompanied by inter- and intramolecular chain transfer. Oxygenated sites may act as weak links for cleavage and the existence of chain branch points may facilitate the transfer process. Polypropylene behaves in a similar manner to polyethylene.

The foregoing discussion applies specifically to olefin addition polymers. Some comments on the thermal behavior of condensation polymers are also appropriate. Polyamides can decompose during melt spinning or molding operations. Such decomposition, usually slight, is apparently initiated by free radicals formed by the homolytic cleavage of $\text{—NH—CH}_2\text{—}$ skeletal bonds. Water and carbon dioxide are also liberated. The water serves to hydrolyze amide (—NH—CO—) linkages, further shortening the chains. Branches are also formed by reaction of terminal —NH_2 groups with carbonyl units (Equation 1.61), leading ultimately to gelation of the molten polymer.



Polyesters, such as poly(ethylene terephthalate), are fairly stable at temperatures just above the melting point. However, at temperatures between 300 and 550°C, this polymer decomposes to yield carbon dioxide, acetaldehyde, and terephthalic acid together with smaller amounts of another decomposition products, such as water, methane, and acetylene.

1.14.2 Ablation

When subjected briefly to very high temperatures, some polymers, such as phenolics, can undergo rapid decomposition to gases and porous char, thereby dissipating the heat and leaving a protective thermal barrier on the substrate. This sacrificial loss of material accompanied by transfer of energy is known as *ablation*. Interaction of a high-energy environment (2,500°C–5,000°C) with the exposed ablative material results in sacrificial erosion of some amount of the surface material, and the attendant energy absorption controls the surface temperature and greatly restricts the flow of heat into the substrate.

Most notable applications of ablative materials are in protecting space vehicles during reentry into the earth's atmosphere, protecting missile nose cones subjected to aerodynamic heating during hypersonic flight in the atmosphere, insulating sections of rocket motors from hot propulsion gases, resisting the intense radiant heat of thermonuclear blasts, and providing thermal protection for structural materials exposed to very high temperatures.

Polymers have been used as ablative materials for a combination of reasons [38]. Some of their advantages are (1) high heat absorption and dissipation per unit mass expended, which may range from several hundred to several thousand calories per gram of ablative material; (2) automatic control of surface temperature by self-regulating ablative degradation; (3) excellent thermal insulation; (4) tailored performance by varying the individual material component and composition of ablative systems; (5) design simplicity and ease of fabrication; (6) light weight and low cost.

Polymer ablatives, however, can be used only for transitory periods of a few minutes or less at very high temperatures and heat load. Moreover, the sacrificial loss of surface material during ablation causes dimensional changes which must be predicted and incorporated into the design.

An ablative material should have a high heat of ablation, which measures the ability of the material to absorb and dissipate energy per unit mass. It should also possess good strength even after charring, since any sloughing off of chunk of material which have not decomposed or vaporized represent poor usage of

the ablative system Figure 1.39 profiles the various stages of heating, charring, and melting in two phenolic composites, one reinforced with glass and the other with nylon. The glass-reinforced system appears to be mechanically superior because it produces a molten glass surface, whereas the nylon-reinforced system may have higher thermal efficiency.

1.14.3 Flame Retardation

All thermoset plastics are self-extinguishing. Among thermoplastics, nylon, polyphenylene oxide, polysulfone, polycarbonate, poly(vinyl chloride), chlorinated polyether, poly(chlorotrifluoroethylene) and fluorocarbon polymers have self-extinguishing properties [39]. The burning characteristics of some polymers are summarized in Table 1.14. Halogenation enhances the flame retardancy of polymers. Thus when the chlorine content of PVC, which usually has 56% chlorine, is increased, as in chlorinated PVC (61% chlorine), the oxygen index increases from 43 to 60. (The oxygen index is a minimum percent of oxygen in a N_2/O_2 gas mixture necessary to support combustion. A material with an oxygen index greater than 27 usually passes the vertical burn test. The burning characteristics of polymers are discussed more fully in Chapter 5.)

A discussion on flame-retardant additives is given in a later section on polymer compounding.

1.15 Deterioration of Polymers

Deterioration of polymers is manifested in loss of strength, loss of transparency, warpage, cracks, erosion, and so on [40–42]. Hydrophilic materials such as nylon or cellulose acetate can undergo swelling at high humidity or shrinkage due to low humidity. Degradation can occur due to imposition of energy in the form of heat, mechanical action, ultrasonic and sonic energy, radiation such as gamma rays, x-rays, visible light, ultraviolet light, infrared, and electrical action in the form of dielectric effects. Deterioration can occur by chemical effects such as oxidation, ozone attack, hydrolysis, attacks by solvents and detergents, cracking due to swelling of the plasticizer, hardening due to loss of the plasticizer, migration of plasticizers from layer to layer, crazing and cracking, delamination or debonding, void formation, etc.

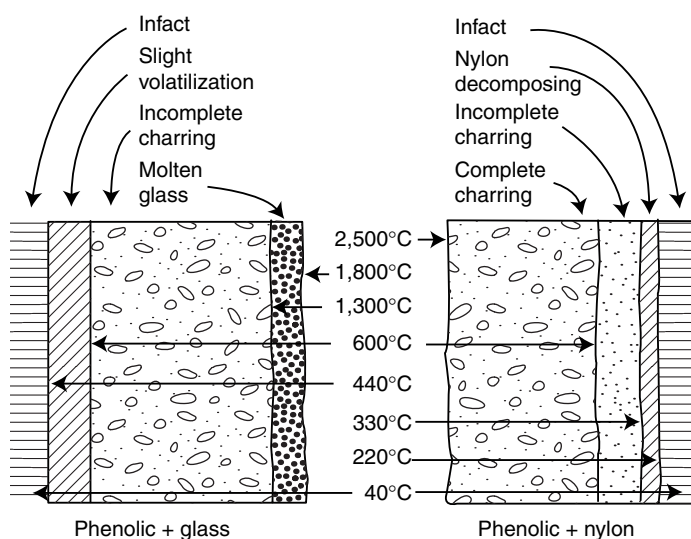


FIGURE 1.39 Temperature distribution in two plastics during steady-state ablation. (After Schmidt, D. L., *Mod. Plastics*, 37, 131 (Nov. 1960), 147 (Dec. 1960).)

TABLE 1.14 Burning Characteristics and Burn Rates of Some Polymers

Polymer	Burning Characteristics	Burn Rate ^a (cm/min)
Polyethylene	Melts, drips	0.8–3.0
Polypropylene	Melts, drips	1.8–4.0
Poly(vinyl chloride)	Difficult to ignite, while smoke	Self-extinguishing
Poly(tetrafluoroethylene)	Melts, chars, bubbles	Nonburning
Fluorinated ethylene propylene copolymer	Does not ignite	Nonburning
Polybutylene	Burns	2.5
Acetal	Burns, bluish flame	1.3–2.8
Cellulose acetate	Burns, yellow flame sooty smoke	1.3–7.6
Cellulose propionate	Burns, drips	1.3–3.0
Cellulose acetate butyrate	Burns, drips	0.8–4.3
Acrylonitrile–butadiene–styrene (general purpose)	Burns	2.5–5.1
Styrene–acrylonitrile	Melts, chars, bubbles	1.0–4.0
Polystyrene	Softens, bubbles, black smoke	1.3–6.3
Acrylic	Burns slowly, drips	1.4–4.0
Nylons	Burns slowly, froths	Self-extinguishing
Phenylene oxide		Self-extinguishing
Polysulfone		Self-extinguishing
Chlorinated polyether		Self-extinguishing
Polyimide		Nonburning

Source: Adapted from Kuryla, W. C. and Papa, A. J., eds. 1973. *Flame Retardancy of Polymeric Materials*, Vol. 3. Marcel Dekker, New York.

^a ASTM D-635 test procedure.

1.15.1 Chemical Deterioration

Liner or thermoplastic polymers may deteriorate by scission. Ultraviolet light and neutrons can easily break a C–C bond of a vinyl-type polymer, producing smaller molecules (Figure 1.40).

Cross-linking is another way that linear or thermoplastic polymers may deteriorate. Two well-known examples are aging of polyethylene and natural rubber, with loss of flexibility due to cross-linking by oxygen under the catalytic action of sunlight (Figure 1.32). Vulcanized rubber has only 5%–20% of its possible positions anchored by sulfur cross-links. Over time there may be further cross-links of oxygen by the air, and the polymer may thus gradually lose its deformability and elasticity.

Because the oxygen molecule is a biradical, its reaction with a polymer usually results in a chain reaction involving free radicals. Thus, a polymer present in air or an atmosphere rich in oxygen can lose an H atom by reacting with O₂ to form a free radical, which then reacts with another oxygen molecule to form

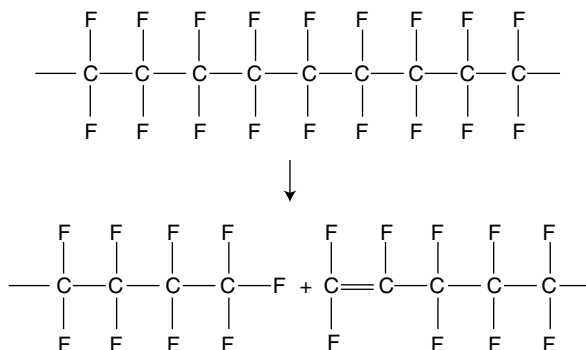
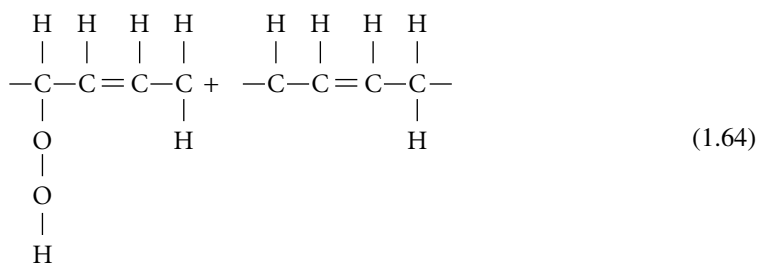
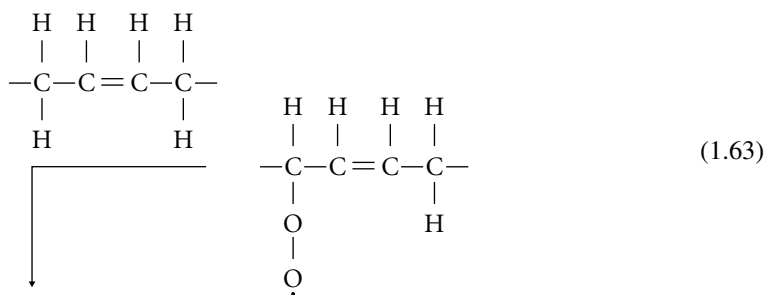
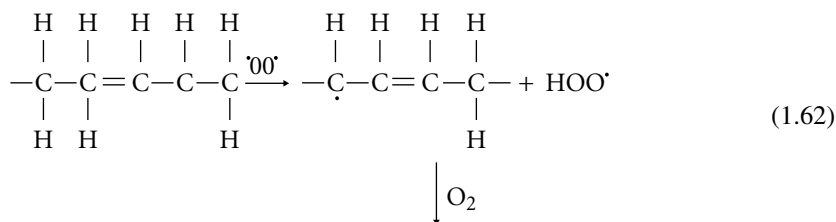
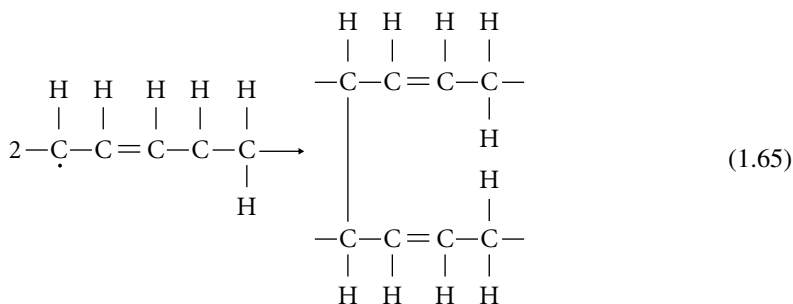


FIGURE 1.40 Scission of polytetrafluoroethylene by irradiation.

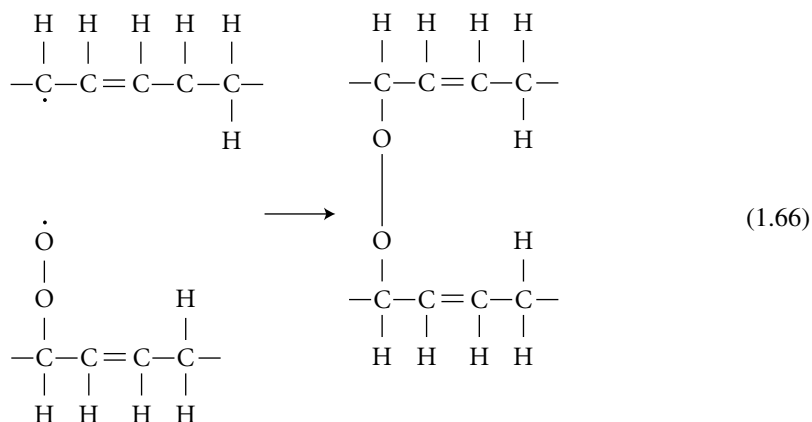
a peroxy free radical. The latter, in turn, reacts with another unit of a polymer chain to produce a hydroperoxide and another free radical.



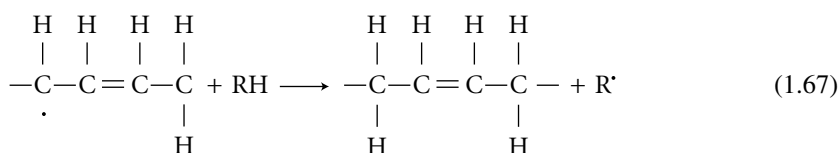
Free radical can combine together and form a stable molecule.



Termination of the chain reaction can also occur with the formation of a peroxide which may be transitory.

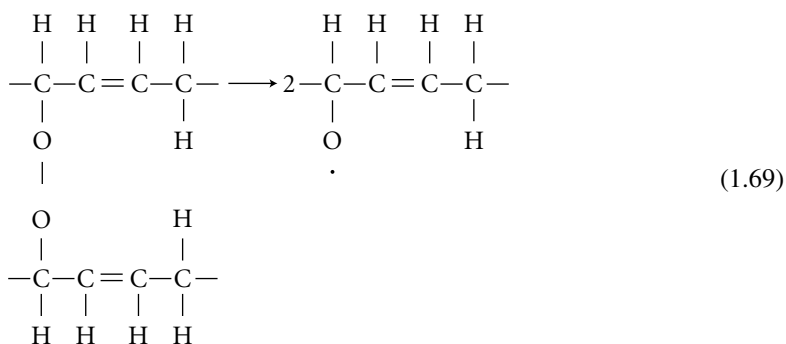
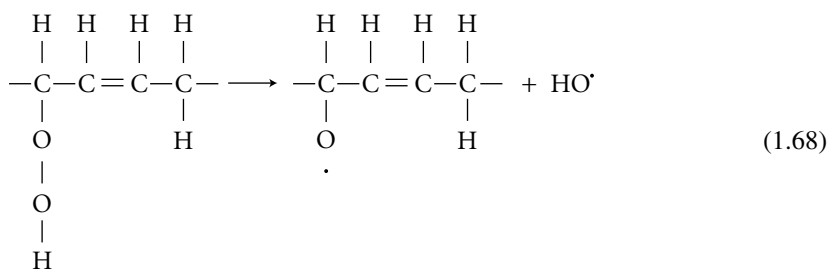


Inhibitors or antioxidants can also stop the process.

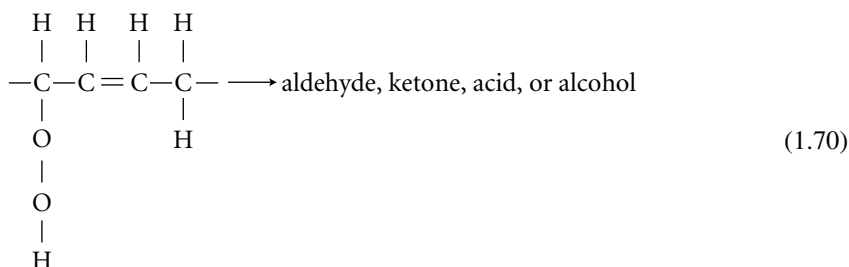


In this way, the chain is broken, and an inactive radical (R') is yielded. Aromatic amines or phenolic compounds can act as inhibitors.

However, new radicals can also be formed from the peroxy groups



Thus for each original reaction with oxygen there can be numerous propagation reaction. The peroxides may also cleave to give aldehydes, ketones, acids, or alcohols. Due to this type of molecular cleavage, the product becomes soft with lower average molecular weight.



Ozone provides a very reactive source of oxygen because it breaks down to an oxygen molecule and a single reactive oxygen.



The temperature resistance of various plastics in air has been summarized in [Figure 1.34](#) and [Table 1.13](#).

Polymers containing hydrolysable groups or which have hydrolysable groups introduced by oxidation are susceptible to water attack. Hydrolyzable groups such as esters, amides, nitriles, acetals, and certain ketones can react with water and cause deterioration of the polymer. The dielectric constant, power factor, insulation resistance, and water absorption are most affected by hydrolysis. For polyesters, polyamides, cellulose, and cellulose either and esters, the hydrolysable groups are weak links in the chain, and hydrolysis of such polymers can cause serious loss of strength. A summary of water absorption characteristics of common plastic and rubbers is presented in [Table 1.15](#).

1.15.2 Degradation by Radiation

It was mentioned earlier that radiation may cause both cross-linking or degradation. Which predominates depends on radiation dosage, polymer structure, and temperature. Ultraviolet (UV) light causes 1,1-disubstituted vinyl polymers to degrade almost exclusively to monomer at elevated temperatures. Whereas cross-linking and chain scission reaction predominate at room temperature. Other vinyl polymers undergo cross-linking primarily, regardless of temperature.

Irradiation with a beam of x-rays, γ -rays, or electrons leads to much higher yields of monomer from 1,1-disubstituted polymers at room temperature. This phenomenon is used advantageously for microetching of resist coatings with electron beams in the preparation of integrated circuits. The process works on the principle that a silicon chip surface will be exposed if an electron beam depolymerizes the protective resin (resist) coating that covers the surface. The exposed silicon can then be doped. Because a beam of high energy radiation has a shorter wavelength than UV light, it is possible to etch finer details in the resist than via the alternative photocross-linking process using UV light. Poly(methyl methacrylate) has been studied extensively as an etch-type resist. This subject is discussed more fully in [Chapter 5](#).

1.15.3 Microbiological Deterioration

One of the main advantages of synthetic polymers over naturally occurring polymeric materials such as cellulose or leather is their resistance to bacterial or fungal attack. Hence, the synthetic materials are, in general, more permanent. However, a few synthetic polymers are susceptible to biological breakdown and it is clearly important to know, from an applications point of view, which polymers are the most susceptible in a biological environment.

Polyurethanes in particular appear to be susceptible to microbial attack, though polyether polyurethanes (see [Chapter 4](#)) are more resistant to biological degradation than are polyester polyurethanes. The precise mechanisms of these degradations are not fully understood. Polyethylene,

polypropylene, polyfluorocarbons, polyamides, polycarbonates, and many other polymer systems appear to be resistant to biological attack.

Table 1.16 provides a qualitative assessment of the resistance of plastic and rubbers to attack by microorganisms. The controversial assessment in certain cases may be due to discrepancies in reported data arising from differences in measurement technique, materials used, average molecular weight of materials, fillers, impurities in polymers, etc.

1.16 Stabilization of Polymers

We have seen that polymers tend to undergo degradation such as chain scission, depolymerization, cross-linking, oxidation, and so on [43–47]. These changes can be effected by various environmental factors such as heat, light, radiation, oxygen, and water. Various stabilizing ingredients are added to plastics to prevent or minimize the degradative effects. These ingredients act either by interfering with degradative processes or by minimizing the cause of degradation.

TABLE 1.15 Water Absorption Characteristics of Plastics and Rubbers

Material	Water abs. (%) 24 h on Sample 3.2 mm Thick
Phenol–formaldehyde resin cast (no filler)	0.3–0.4
Phenol–formaldehyde resin molded (wood–four filler)	0.3–1.0
Phenol–formaldehyde resin molded (mineral filler)	0.01–0.3
Phenol–furfural resin (wood–flour filler)	0.2–0.6
Phenol–furfural resin (mineral filler)	0.2–1.0
Urea–formaldehyde resin (cellulose filler)	0.4–0.8
Melamine–formaldehyde resin (cellulose filler)	0.1–0.6
Melamine–formaldehyde resin (asbestos filler)	0.08–0.14
Ethyl cellulose	0.8–1.8
Cellulose acetate (molding)	1.9–6.5
Cellulose acetate (high acetyl)	2.2–3.1
Cellulose acetate–butyrate	1.1–2.2
Cellulose nitrate	1.0–2.0
Casein plastics	7–14
Poly(vinyl chloride) (plasticized)	0.1–0.6
Poly(vinylidene chloride) (molding)	< 0.1
Poly(vinyl chloride acetate) (rigid)	0.07–0.08
Poly(vinyl chloride acetate) (flexible)	0.40–0.65
Poly(vinyl formal)	0.6–1.3
Poly(vinyl butyral)	1.0–2.0
Allyl resins (cast)	0.3–0.44
Polyester resins (rigid)	0.15–0.60
Polyester resin (flexible)	0.1–2.4
Poly(methyl methacrylate)	0.3–0.4
Polyethylene	< 0.01
Polypropylene	0.01–0.1
Polystyrene	0.03–0.05
Polytetrafluoroethylene	0.00
Nylon (molded)	1.5
Rubbers (extruded)	0.4
Chlorinated rubber	0.1–0.3

Source: Data mainly from Halim Hamid, S., Amin, M. B., and Maadhah, A. G., eds. 1992. *Handbook of Polymer Degradation*. Marcel Dekker, New York.

TABLE 1.16 Resistance of Plastics and Rubbers to Attack by Microorganisms

	Resistance
Plastics	
Poly(methyl methacrylate)	Good
Polyacrylonitrile (orlon)	Good
Acrylonitrile-vinylchloride copolymer (Dynel)	Good
Cellulose acetate	Good, poor
Cellulose acetate butyrate	Good
Cellulose acetate propionate	Good
Cellulose nitrate	Poor
Ethyl cellulose	Good
Acetate rayon	Good
Viscose rayon	Poor
Phenol-formaldehyde	Good
Melamine-formaldehyde	Good, poor
Urea-formaldehyde	Good
Nylon	Good
Ethylene glycol terephthalate (Terylene)	Good
Polyethylene	Good, questionable
Polytetrafluoroethylene (Teflon)	Good
Polymonochlorotrifluoroethylene	Good
Polystyrene	Good
Poly(vinyl chloride)	Good, questionable
Poly(vinyl acetate)	Poor
Poly(vinyl butyral)	Good
Glyptal resins (alkyd resins)	Poor, moderate
Silicone resins	Good
Rubbers	
Pure natural rubber (caoutchouc)	Attacked
Natural rubber vulcanizate	Attacked
Crude sheet	Attacked
Pale crepe, not compounded	Attacked
Pale crepe, compounded	Resistant, attacked
Smoked sheet, not compounded	Attacked
Smoked sheet, compounded	Resistant, attacked
Reclaimed rubber	Attacked
Chlorinated rubber	Resistant
Neoprene, compounded	Resistant
GR-S, butadiene-styrene, compounded	Resistant, attacked
Hycar OR, butadiene-acrylonitrile compounded	Resistant, attacked
Buna N, butadiene-acrylonitrile, compounded	Attacked
GR-I (butyl), isobutylene-isoprene, compounded	Resistant, attacked
Thiokol, organic polysulfide, uncured	Attacked
Thiokol, organic polysulfide, vulcanized	Resistant
Thiokol, organic polysulfide, sheets for gasoline tank lining	Attacked
Silicone rubber	Resistant

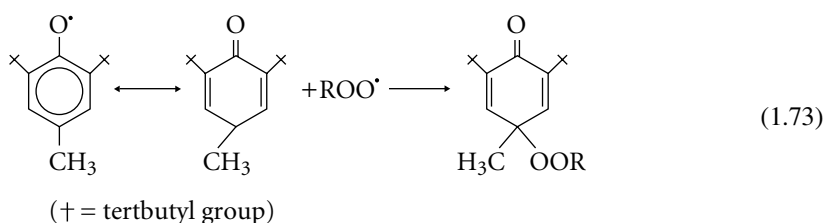
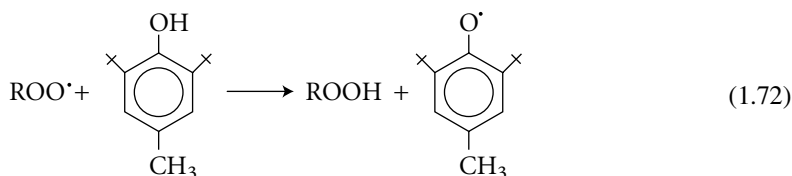
Source: Adapted from Halim Hamid, S., Amin, M. B., and Maadhah, A. G., eds. 1992. *Handbook of Polymer Degradation*. Marcel Dekker, New York.

1.16.1 Antioxidants and Related Compounds

Oxidation, as we have noted, is a free-radical chain process. The most useful stabilizing agents will therefore be those which combine with free radicals, as shown by Equation 1.67, to give a stable species incapable of further reaction. These stabilizing agents are called antioxidants. They are the most frequently employed ingredients in plastics, fibers, rubbers, and adhesives. Stabilization is also achieved in some polymer systems by the use of additives which moderate the degradation reaction.

Two large, basic groups of antioxidants are normally distinguished: (1) chain terminating or primary antioxidants, and (2) hydroperoxide decomposers or secondary antioxidant, frequently called synergists.

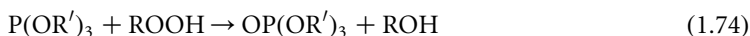
The majority of primary antioxidants are sterically hindered phenols or secondary aromatic amines. They are capable of undergoing fast reaction with peroxy radicals and so are often called radical scavengers. For hindered phenols, for example, such reactions may be represented by the following scheme:



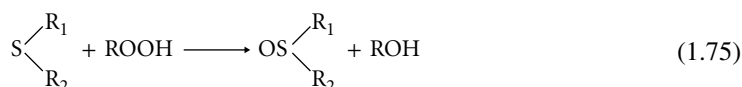
Stabilization is achieved by the fact that Reaction 1.72 competes with peroxy radical reactions in polymer degradation, such as Reaction 1.64, transforming the reactive peroxy radical into a much less reactive phenoxyl radical, which, in turn, is capable of reacting with a second peroxy radical according to Reaction 1.73.

The phenoxyl radicals formed in Reaction 1.72 do not initiate new radical chains at the normal temperatures of use and testing, but such propagation reactions become possible at high temperatures. The thermal stability of peroxycyclohexadienones (formed by Reaction 1.73) is also limited, and their decomposition leads to new reaction chains. The effectiveness of sterically hindered phenols thus decreases with increasing temperature.

The secondary antioxidants are usually sulfur compounds (mostly thioethers and esters of thiodipropionic acid) or trimesters of phosphorous acid (phosphates). A remedy for many types of discoloration in plastics is often the use of a phosphite or a thioether. Both have the ability to react with hydroperoxides, as those formed in Reaction 1.72, to yield nonradical products, following heterolytic mechanisms. The reaction of phosphites to phosphates as an example:



Thioethers react with hydroperoxides in a first stage to yield sulfoxides and alcohols:



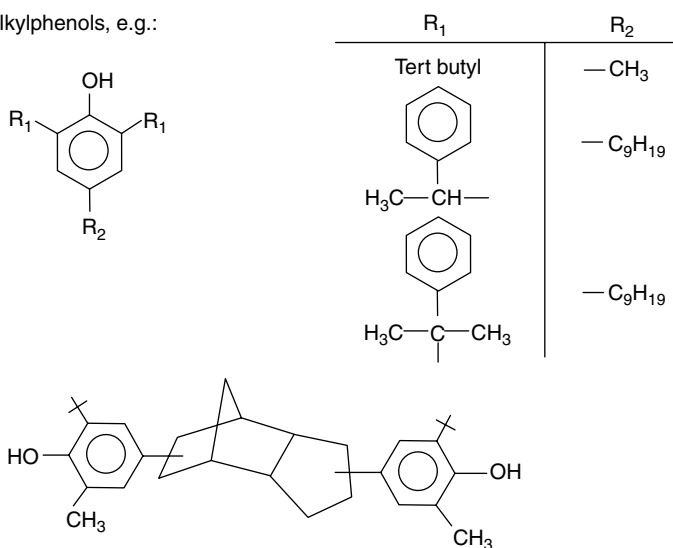
Sulfoxides themselves yield, on further oxidation, even more powerful hydroperoxide decomposers than the original sulfides, in that they are able to destroy several equivalents of hydroperoxides. This catalytic effect is explained by the intermediate occurrence of sulfenic acids and sulfur dioxide. The fact that the phenomenon of synergism, which is defined as a cooperative action such that the total effect is greater than the sum of two or more individual effects taken independently, is often observed when primary and secondary antioxidants are combined has been explained with the concept of the simultaneous occurrence of the radical reactions (e.g., Equation 1.72) and the nonradical hydroperoxide decomposition (e.g., Equation 1.74 and Equation 1.75).

The preceding synergistic effect may be considered as an example of heterosynergism, which arises from the cooperating effect of two or more antioxidants acting by different mechanisms. Homosynergism, on the other hand, involves two compounds of unequal activity that are operating by the same mechanism, for example, a combination of two different chain-breaking antioxidants that normally function by donation of hydrogen to a peroxy free radical. The most likely mechanism of synergism in this case would involve the transfer of hydrogen from one inhibitor molecule to the radical formed in the reaction of the other inhibitor with a peroxy radical (see Equation 1.72), thus regenerating the latter inhibitor and prolonging its effectiveness.

1.16.2 Chemical Structures of Antioxidants

While sterically hindered phenols and secondary aromatic amines are the two main chemical classes of antioxidants for thermoplastics, the greatest diversity is, however, found in the class of the sterically hindered phenols. Most of these phenols are commercially available as relatively pure chemicals. Although aromatic amines are often more powerful antioxidants than phenols, their application is

(a) Alkylphenols, e.g.:



(b) Alkylidene-bisphenols, e.g.:

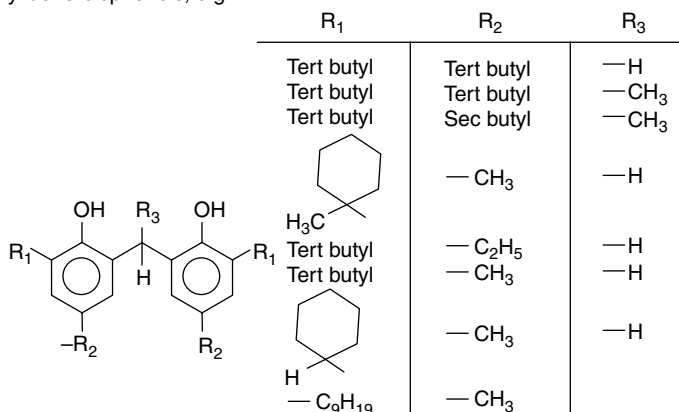


FIGURE 1.41 Structural formulas [45] of important sterically hindered phenols used as antioxidants for thermoplastics.

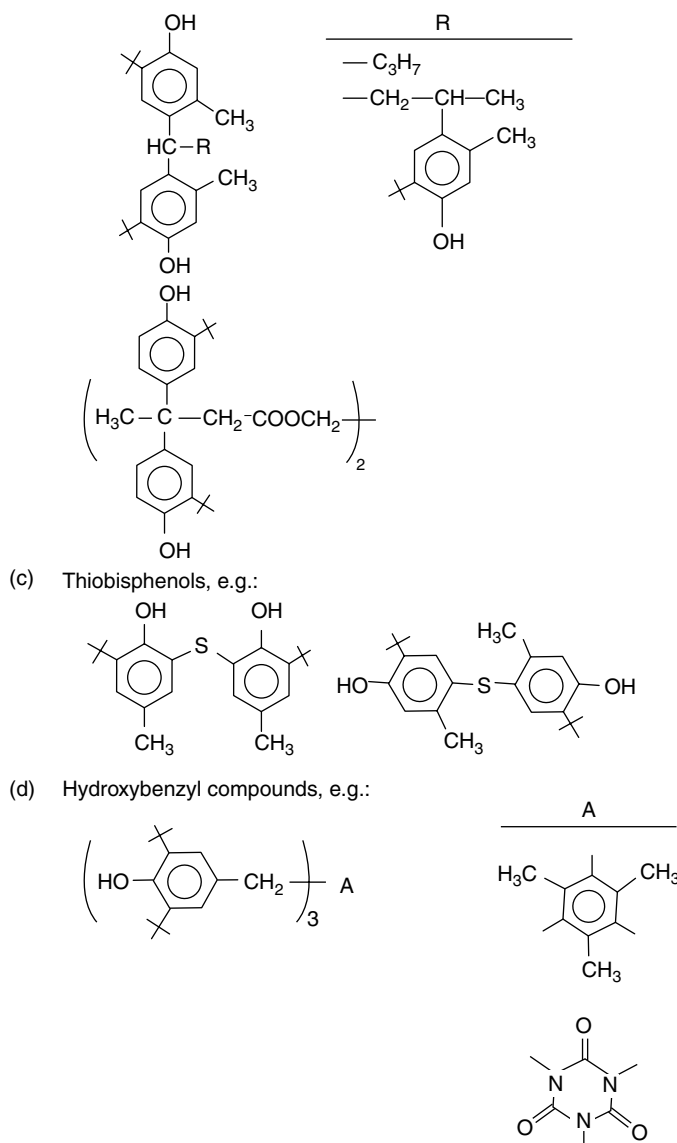


FIGURE 1.41 (continued)

limited to vulcanized elastomers since the staining properties of aromatic amines prohibit their use in most thermoplastics.

Sterically hindered phenols of commercial importance may be further classified, according to their structure, into (1) alkylphenols, (2) alkylidene-bisphenols, (3) thiobisphenols, (4) hydroxybenzyl compounds, (5) acylaminophenols, and (6) hydroxyphenyl propionates.

An important goal of antioxidant research has been to provide poly-phenols of high molecular weight and low volatility. Most of the commercial sterically hindered phenols have molecular weights in the range 300–600 and above 600. Figure 1.41 depicts structural formulas [45] of the important sterically hindered phenols used as antioxidants.

The majority of secondary antioxidants are esters of thiodipropionic acid with fatty alcohols and trimesters of phosphorus acid. Their chemical structures are shown in Figure 1.42. Phosphites are more

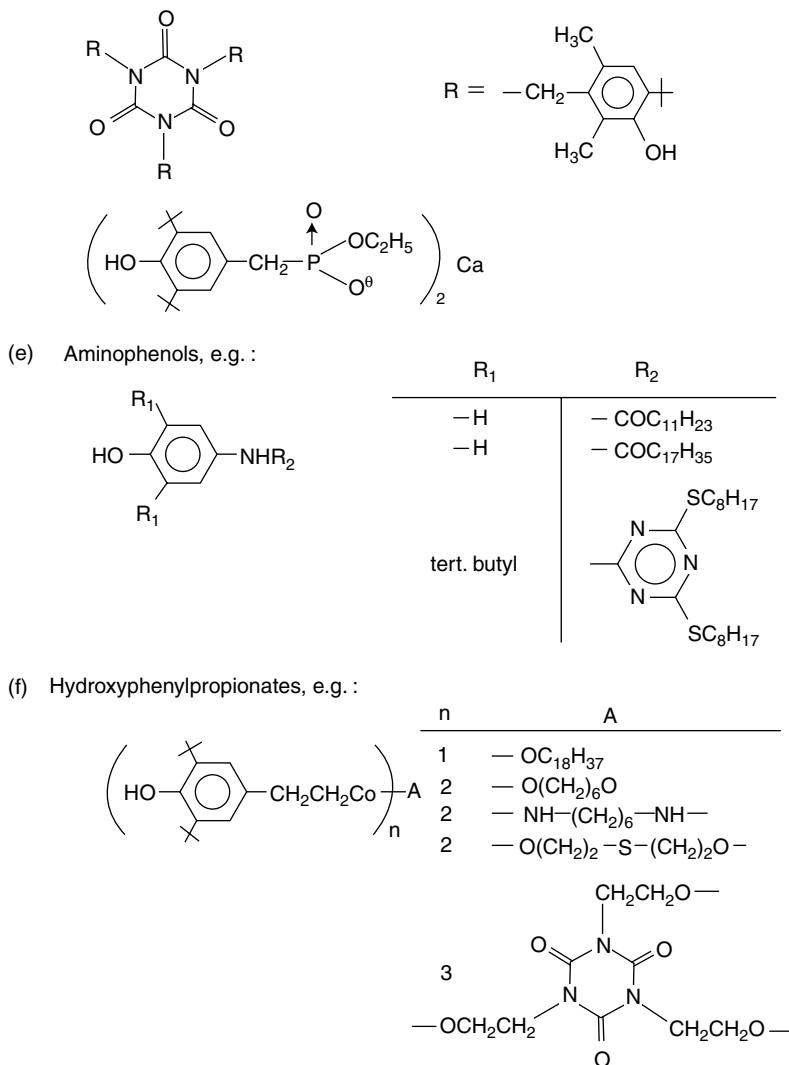


FIGURE 1.41 (continued)

sensitive towards hydrolysis than esters of carboxylic acids, and this point has to be taken into account when storing and using phosphates. Aromatic phosphates are often preferred since they are inherently more resistant to hydrolysis than aliphatic phosphates.

An index of trade names, manufacturers, and suppliers based on a choice of representative antioxidants for thermoplastics is given in [Appendix A3](#). Detailed lists are found in Ref. [45,46].

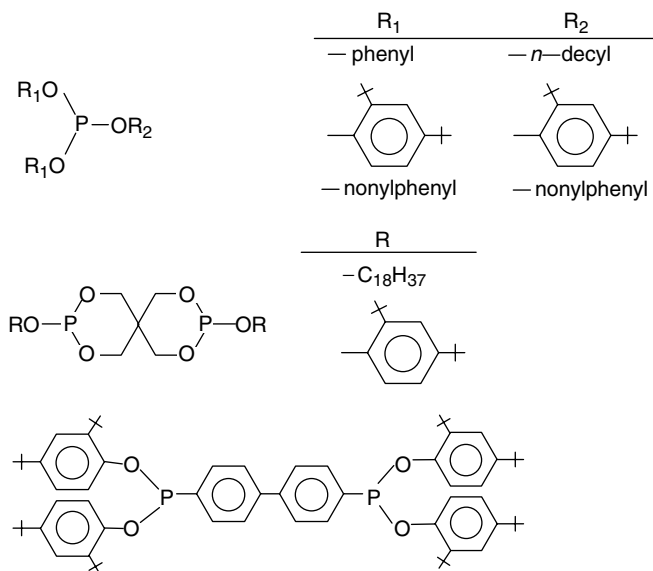
1.16.3 Stabilization of Selected Polymers

Two important considerations in selecting antioxidants for polymers are toxicity and color formation. Thus, for use in food wrapping, any antioxidant or additive must be approved by the appropriate government agency. An antioxidant widely used in food products and food wrapping is butylated hydroxytoluene (BHT) (see [Figure 1.41a](#): R₁=*tert*-butyl and R₂=-CH₃). It is also added in small amounts to unsaturated raw rubbers before shipping to protect them during storage.

- (a) Thioethers, e.g.:



- (b) Phosphites and phosphonites, e.g.:



- (c) Zinc dibutyldithiocarbamate

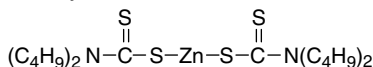
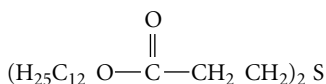


FIGURE 1.42 Structural formulas [45] of some commercial secondary antioxidants for thermoplastics.

Materials that are not effective inhibitors when used alone may nevertheless be able to function as synergists by reacting with an oxidized form of an antioxidant to regenerate it and thus prolong its effectiveness. For example, carbon black forms an effective combination with thiols, disulfides, and elemental sulfur, even though these substances may be almost completely ineffective alone under comparable conditions. Synergistic combinations from a variety of chain terminators and sulfur compounds have been reported. A widely used combination of stabilizers for polyolefins is 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Figure 1.41a) with dilauryl thiodipropionate (DLTDP):



This combination is of particular interest because both components are among the small group of stabilizers approved by the U.S. Food and Drug Administration for use in packaging materials for food products.

Other synergistic combinations have been reported involving free-radical chain terminators used with either ultraviolet absorbers or metal deactivators as the preventive antioxidants. The differences in

mechanism of action of these different types of stabilizers permit them to act independently but cooperatively to provide greater protection than would be predicted by the sum of their separate effects.

1.16.3.1 Polypropylene

Because of the presence of tertiary carbon atoms occurring alternately on the chain backbone, propylene is particularly susceptible to oxidation at elevated temperatures. Since polypropylene is normally processed at temperatures between 220 and 280°C, it will degrade under these conditions (to form lower-molecular-weight products) unless it is sufficiently stabilized before it reaches the processor. The antioxidants are added at least partially during the manufacturing process and at the least during palletizing. Antioxidant systems in technical use are composed of processing stabilizers, long-term heat stabilizers, calcium- or zinc-stearate, and synergists if necessary.

Typical processing stabilizers for polypropylene and butylated hydroxy-toluene (BHT) as the primary antioxidant and phosphates and phosphonates as secondary antioxidants. Examples of the latter that are commonly used are: tetrakis-(2,4-di-*tert*-butyl-phenyl)-4-4'-bisphenylenediphosphonite, distearyl-pentaerythrityl-diphosphonite, tris-(nonylphenyl)-phosphite, tris-(2,4-di-*tert*-butyl-phenyl)-phosphite and bis(2,4-di-*tert*-butyl-phenyl)-pentaerythrityl-diphosphite. In commercial polypropylenes, phosphorous compounds are always used together with a sterically hindered phenol. The compounds are commonly added in concentrations between 0.05 and 0.25%.

The most important long-term heat stabilizers for polypropylene are phenols of medium (300–600) and especially high (600–1,200) molecular weight, which are frequently used together with thioethers as synergists, e.g., dilauryl thiodipropionate (DLTDP), or distearyl thiodipropionate (DSTDP), or dioctadecyl disulfide.

1.16.3.2 Polyethylene

High-density polyethylenes (HDPE) are less sensitive to oxidation than polypropylene, so lower stabilizer concentrations are generally sufficient. As in polypropylene, antioxidants can be added during a suitable stage of manufacture or during palletizing. The antioxidants in technical use are the same as for polypropylene. Phenols of medium- and high-molecular weight are also active as long-term heat stabilizers. Concentrations between 0.03 and 0.15% are usual.

Low-density polyethylene (LDPE) is extensively used for the manufacture of films. During processing, which is carried out at temperatures of approximately 200°C, cross-linking, and thus formation of gel, can occur through oxidation if the polymer is not stabilized. Such gel particles are visible in the film as agglomerates, known as fish eyes or arrow heads. The processing stabilizers used in LDPE consist of systems commonly used for polypropylene, namely, combinations of a phosphite or phosphonite and a long-term heat stabilizer (hindered phenol) in overall concentrations up to 0.1%. Concentrations seldom exceed 0.1%, since the compatibility of any additive in LDPE is considerably lower than in any other polyolefins.

For primary cable insulation. Cable jackets and pipes manufactured from LDPE, medium to high-molecular-weight grades are used and are frequently cross-linked after processing. Long-term heat stabilizer is of primary importance in these applications, since lifetimes of up to 50 years are required (usually at elevated temperatures with short-time peaks up to 100°C for cables). The antioxidants have to be extremely compatible and resistant to extraction. Some typical antioxidants customary for insulation are as follows:

For power cable insulation. Pentaerythrityltetrakis-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate, polymeric 2,2,4-trimethyl-1,2-dihydroquinoline, 4,4'-thiobis-(3-methyl-6-*tert*-butyl-phenol), 2,2'-thiodiethyl-bis-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate, and distearyl thiodipropionate are used as synergists.

For communication cable insulation. 2,2'-Thiobis-(4-methyl-6-*tert*-butyl-phenol), 4,4'-thiobis-(3-methyl-6-*tert*-butyl-phenol), 2,2'-methylene-bis-(4-methyl-6- α -methylcyclohexyl-phenol), 1,1,3-tris-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)-butane, 2,2'-thiodiethyl-bis-3-(3,5-di-*tert*-butyl-4-

hydroxy-phenyl)-propionate, pentaerythrityl-tetrakis-3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl)-propionate, and dilauryl thiodipropionate are used as synergists.

The simultaneous use of metal deactivators has become increasingly important for cable insulation. This is discussed later.

1.16.3.3 Polystyrene

Unmodified crystal polystyrene is relatively stable under oxidative conditions, so that for many applications the addition of an antioxidant is not required. Nevertheless, repeated processing may lead to oxidative damage of the material, leading to an increase of melt flow index and to embrittlement of the material. Stabilization is effected by the addition of octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl)-propionate at concentrations of up to 0.15%, if necessary in combination with phosphates or phosphonites to improve color.

Compared to unmodified crystal polystyrene, impact polystyrene consisting of copolymers of styrene and butadiene are more sensitive to oxidation. This sensitivity is a consequence of the double bonds in polybutadiene component and manifests itself in yellowing and the loss of mechanical properties of the polymer. In impact polystyrene, the following antioxidants or their mixture are used in total concentrations of 0.1%–0.25%: BHT, octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate, 1,1,3-tris-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)-butane, and dilauryl thiodipropionate.

1.16.3.4 Acrylonitrile–Butadiene–Styrene Copolymers

Like impact polystyrene, acrylonitrile–butadiene–styrene copolymers (ABS) are sensitive to oxidation caused by the unsaturation of the elastomeric component. The processes for the manufacture of ABS require the drying (at 100°C–150°C) of powdery polymers that are extremely sensitive to oxidation. Thus, antioxidants have to be added before the coagulation step, normally in emulsified form, although sometimes in solution. The primary antioxidants are frequently used together with a synergist. Primary anti-oxidants commonly used for ABS are BHT, 2,2'-methylenebis-(4-ethyl or methyl-6-*tert*-butylphenol), 2,2'-methylenebis-(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis-(4-methyl-6-nonylphenol), octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate, and 1,1,3-tris-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)-butane. Important synergists are tris-(nonylphenyl)-phosphite and dilauryl thiodipropionate. These antioxidants are either liquids or show comparatively low melting points, which is an important prerequisite for the formation of stable emulsions.

1.16.3.5 Polycarbonate

Thermoxidative degradation of polycarbonate manifests itself in yellowing that is readily seen because of the transparency of polycarbonate. For this reason, stabilization against discoloration is considered to be important. Severe requirements are also imposed on the nonvolatility and thermostability of the stabilizers for polycarbonate, because the processing temperatures are extraordinarily high (about 320°C). The stabilizers are generally added during the palletizing step.

Yellowing of polycarbonate during processing is retarded by the addition of phosphates or phosphonites. They are used in concentrations of 0.05%–0.15%, possibly in combination with an epoxy compound as acid acceptor. The addition of these stabilizers not only decreases the yellowness index but also inhibits the rise of the melt flow index and negative influence on impact strength of processing.

The effective processing stabilizers are not suitable, however, for preventing the aging effect of long-term use. For long-term heat stabilization, a sterically hindered phenolic antioxidant is added. An effective antioxidant is octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate.

1.16.3.6 Nylons

Degradation of nylons due to processing and aging causes discoloration and loss of mechanical properties, although not at the same rate. For example, yellowing is observed already after short periods of oven aging at 165°C, but tensile strength and elongation are hardly affected during the same time period. Discoloration of polyamides during processing can be suppressed to a certain extent by the addition of phosphates, e.g., tris-(2,4-di-*tert*-butylphenyl)-phosphite, in concentrations of 0.2%–0.4%.

The stabilization of nylons is mainly a matter of long-term stabilization. Three main groups of stabilizers have become known: (1) copper salts, especially in combination with halogen and/or phosphorus compounds (e.g., copper acetate + potassium iodide/phosphoric acid), (2) aromatic amines (e.g., *N,N'*-dinaphthyl-*p*-phenylenediamine or *N*-phenyl-*N'*-cyclohexyl-*p*-phenylenediamine), and (3) hindered phenols.

Copper-halogen systems are effective in very low concentrations (10–50 ppm of copper; approximately 1000 ppm of halogen), although they are extracted quite easily with water and cause discoloration of the substrate. Next to the copper-halogen systems, aromatic amines are the most effective stabilizers. They are used in rather high concentrations, from 0.5 to 2%. However, since they have strongly discoloring properties they are used mainly for technical articles, which tolerate discoloration.

Hindered phenols do not show the above-mentioned disadvantages. They are the stabilizers of choice whenever good oxidation stability has to be coupled with good color stability and, possibly, food approval of the end article. The most important hindered phenols in use are the following: *N,N'*-hexamethylenebis-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionamide, 1,1,3-tris-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)-butane, 1,3,5-tris-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-mesitylene, and BHT. The antioxidants can be added already during polycondensation, the normal concentration ranging from 0.3 to 0.7%.

1.16.3.7 Thermoplastic Elastomers

Styrene-based thermoplastic elastomers (see [Chapter 4](#)) are sensitive to oxidation since they contain unsaturated soft segments. These elastomers are manufactured by solution polymerization process in aliphatic hydrocarbons. In order to prevent autoxidation during the finishing steps (stripping, drying), which manifests itself by a rise in melt flow index and discoloration of the raw polymer, antioxidant is added to the polymer solution before finishing. Hence the antioxidant has to be soluble in the polymerization solvent.

A number of hindered phenols are used in practice in a total concentration of approximately 0.5%. Examples of primary antioxidants used are BHT, 1,3,5-tris-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-mesitylene, and octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate. Tris-(nonylphenyl)-phosphite is used as a synergist. BHT may, however, be partially lost during finishing and drying. The phenols of higher molecular weight are used as they have low volatility and have the further advantage of protecting the material also during processing and end use.

Thermoplastic polyester elastomers (see [Chapter 4](#)) contain readily oxidizable polyether soft segments that make stabilization necessary. Essentially two antioxidants, namely, 4,4'-di(α,α -dimethylbenzyl)-diphenylamine and *N,N'*-hexamethylenebis-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionamide are in use in concentrations of up to 1%. The antioxidants can be added during pelletizing, or even better, already during polycondensation. When added during polycondensation, *N,N'*-hexamethylenebis-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionamide is partly chemically bound to the polymer because of its amide structure. The antioxidant thus becomes highly stable to extraction.

The oxidative stability of thermoplastic polyurethane elastomers is determined by the length and the structure of the linear polyether or polyester soft segments. The stability of polyether urethanes against autoxidation is distinctly lower compared to that of polyester urethanes, but the latter are less stable to hydrolysis. Antioxidants may be used in polyurethanes for stabilization against loss of mechanical properties and against discoloration in injection molding grades and as gasfading inhibitors in elastomeric fibers.

The antioxidant used in thermoplastic polyurethane elastomers are hindered phenols, e.g., BHT, octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate, and pentaerythrityl-tetrakis-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate, and aromatic amines, e.g., 4,4'-di-*tert*-octyl-diphenylamine, as well as their combinations. Aromatic amines can, however, be employed only in very limited concentrations (250–550 ppm at most) because of their discoloring properties.

1.16.3.8 Polyacetal

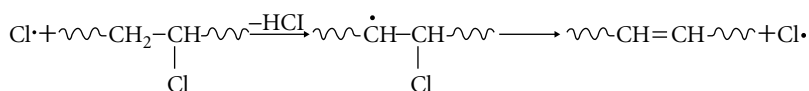
Polyoxymethylenes have a marked tendency to undergo thermal depolymerization with loss of formaldehyde. To prevent thermal depolymerization, polyoxymethylenes are structurally modified, the two possibilities being acetylation to block the reactivity of the end groups of co-polymerization with cyclic ethers, e.g., ethylene oxide. Polyacetals are also sensitive towards autoxidation, which invariably leads to depolymerization as a result of chain scission. The formaldehyde released by depolymerization is very likely to be oxidized to formic acid, which can catalyze further depolymerization.

The stabilizer systems for polyacetals are invariably composed of a hindered phenol with a costabilizer. The hindered phenols in use are 2,2'-methylenebis-(4-methyl-6-*tert*-butyl-phenol), 1,6-hexamethylenebis-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate, and pentaerythrityl-tetrakis-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate. A large number of nitrogen-containing organic compounds have been described as costabilizers for polyacetals, e.g., dicyandiamide, melamine, terpolyamides, urea, and hydrazine derivatives. The effectiveness of these compounds is based on their ability to react with formaldehyde and to neutralize acids, especially formic acid, formed by oxidation. In addition to nitrogen compounds, salts of long-chain fatty acids (e.g., calcium stearate, calcium ricinoleate, or calcium citrate) are also used as acid acceptors. The practical concentrations are 0.1–0.5% for the phenolic antioxidant and 0.1–1.0% for the costabilizer.

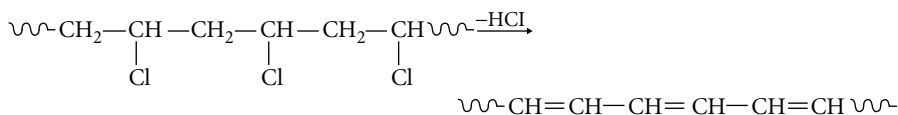
1.16.3.9 Poly(Vinyl Chloride)

Poly(vinyl chloride) (PVC) is relatively unstable under heat and light. The first physical manifestation of degradation is a change in the PVC color, which on heating, changes from the initial water-white to pale yellow, orange, brown, and finally black. Further degradation causes adverse changes in mechanical and electrical properties.

The most widely accepted mechanism for PVC degradation is one based on a free-radical chain. Thermal initiation probably involves loss of a chlorine atom adjacent to some structural abnormality, such as terminal unsaturation, which reduces the stability of the C–Cl bond [44]. The chlorine radical thus formed abstracts a hydrogen to form HCl, and the resulting chain radical then reacts to form a chain unsaturation with regeneration of another chlorine radical.



Thus, as hydrogen chloride is removed, polyene structures are formed:



The reaction can also be initiated by ultraviolet light. In the presence of oxygen the reactions are accelerated (as evidenced by the acceleration of color formation), and ketonic structures are formed in the chain.

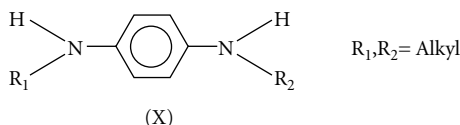
Stabilizers are almost invariably added to PVC to improve its heat and light stability. The species found effective in stabilizing PVC are those that are able to absorb or neutralize HCl, react with free radicals, react with double bonds, or neutralize other species that might accelerate degradation. Lead compounds, such as basic lead carbonate and tribasic lead sulfate, and metal soaps of barium, cadmium, lead, zinc, and calcium are used as stabilizers. Obviously, they can react with HCl. Epoxy plasticizers aid in stabilizing the resin. Another group of stabilizers are the organotin compounds, which find application because of their resistance to sulfur and because they can yield crystal-clear compounds.

1.16.3.10 Rubber

In stabilizing rubber, antioxidants are classified as staining or nonstaining, depending on whether they develop color in use. In carbon-black-loaded rubber tire a staining material is not harmful. For white rubber goods, however, it is important that the additives used be colorless and that they stay colorless while protecting against oxidation. Some antioxidants that find use in rubber are phenyl- β -naphthylamine (PBNA), which is staining, and 2,2'-thiobis (6-*tert*-butyl-para-cresol) (see Figure 1.41c), which is nonstaining.

It has been established that ozone formation is a general phenomenon that occurs when free radicals can combine with oxygen. Rubber products made from natural rubber, styrene-butadiene rubber (SBR), or nitrile rubber, when stretched moderately and exposed to low concentrations of ozone, crack rapidly and sometimes disastrously. The cracking is caused by cuts that appear on the surface and may penetrate deeply, causing serious damage. These cuts appear only when the rubber is under tension during exposure to ozone and if they cross the lines of tension at an angle of 90°. Since the cracking problem is associated only with elastomers containing some degree of residual unsaturation, the process is considered to be related to the attack of ozone on the unsaturation. Unlike molecular oxygen (O₂), ozone appears to add directly to the double bond, which is often followed by chain scission. Use of diene rubbers in an environment containing ozone, such as an automobile tire in some urban locations, therefore calls for stabilization against ozone.

The effect of ozone is both greatly delayed and reduced when various antiozonants, such as *N,N'*-di-alkyl-*p*-phenylene-diamines (X) or similar compounds, are incorporated in the rubber. They may react directly with ozone or with the ozone-olefin reaction products in such a way as to prevent chain scission. SBR is much more receptive to protection than either the nitrile or natural rubbers. Of the latter two the nitrile is more readily inhibited. If a wax is also added in small quantities with the antiozonant, the retardation of the attack of ozone is in certain instances enhanced several fold.



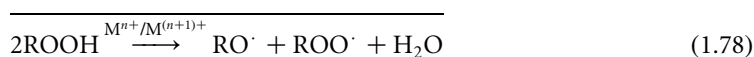
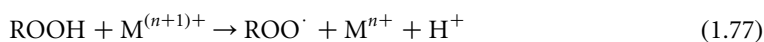
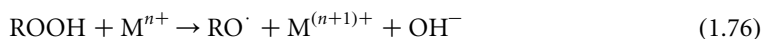
It is believed that waxes function by providing an unreactive layer on the rubber surface. Since, unlike oxygen, ozone reacts only at the surface and does not diffuse into the sample, a surface layer of relatively unreactive wax presents an impervious surface to ozone. The wax thus needs to bloom (i.e., exude to the surface) in order to afford protection. A great deal of attention has therefore been paid to the factors affecting migratory aptitude of wax. Waxes with good protective power have been found to have melting points between 65 and 72°C, refractive indices in the range of 1.432–1.438, and branching to the extent of 30%–50% side chains [44].

Of the two general categories of waxes—paraffin and micro-crystalline—the latter are more strongly held to the surface. However, the use of waxes alone to provide protection against ozone attack is rather well restricted to static conditions of service. Whenever constant flexing is present, even the more strongly held microcrystalline waxes flake off and protection is lost. Combinations of waxes and chemical antiozonants are therefore used to provide protection under both static and dynamic conditions of service. In fact, it is felt that waxes can aid in the diffusion of chemical antiozonant to the rubber surface.

1.17 Metal Deactivators

As described previously, thermooxidative degradation of polyolefins proceeds by a typical free-radical chain mechanism in which hydroperoxides are key intermediates because of their thermally-induced hemolytic decomposition to free radicals, which in turn initiate new oxidation chains. However, since the monomolecular hemolytic decomposition of hydroperoxides into free radicals require relatively high activation energies, this process becomes effective only at temperatures in the range of 120°C and higher.

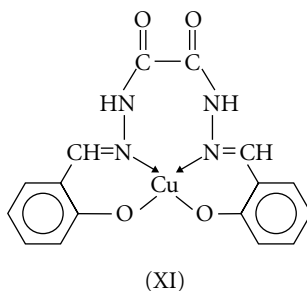
But in the presence of certain metal ions, hydroperoxides can undergo catalytic decomposition even at room temperature by a redox reaction to radical products. Two oxidation-reduction reactions can be involved depending on the metal and its state of oxidation:



The electron transfer producing free radicals as shown above is preceded by the formation of unstable coordination complexes of the metal ions with alkyl hydroperoxides. The relative importance of Reaction 1.76 and Reaction 1.77 depends upon the relative strength of the metal ion as an oxidizing or reducing agent. When the metal ion has two valence states of comparable stability, both Reaction 1.76 and Reaction 1.77 will occur, and a trace amount of the metal can convert a large amount of peroxide to free radicals according to the sum of the two reactions (Reaction 1.78). This is true of compounds of metals such as Fe, Co, Mn, Cu, Ce, and V, commonly called transition metals.

The presence of the above-mentioned metal ions increases the decomposition rate of hydroperoxides and the overall oxidation rate in the autoxidation of a hydrocarbon to such an extent that even in the presence of antioxidants, the induction period of oxygen uptake is drastically shortened. In such a case, sterically hindered phenols or aromatic amines even at rather high concentrations, do not retard the oxidation rate satisfactorily. A much more efficient inhibition is then achieved by using metal deactivators, together with antioxidants. Metal deactivators are also known as copper inhibitors, because, in practice, the copper-catalyzed oxidation of polyolefins is by far of greatest importance. This is due to the fact that polyolefins are the preferred insulation material for communication wire and power cables, which generally contain copper conductors.

The function of a metal deactivator is to form an inactive complex with the catalytically active metal species. Specially suited for this purpose are chelating agents, which can form metal complexes of high thermal stability. The general feature of chelating agents is that they may contain several ligand atoms like N, O, S, P, alone or in combination with functional groups such as hydroxyl, carboxyl, or carbamide groups. The chelating agent *N,N'*-bis-(*o*-hydroxybenzal) oxalyldihydrazide is a good example for the above mentioned structural possibilities. It forms a soluble complex (XI) with the first mole of a copper salt by binding at the phenolic group, and a second mole of copper salt binds at amide nitrogens to form an insoluble complex.



Besides their main function to retard efficiently the metal-catalyzed oxidation of polyolefins, metal deactivators have to possess a number of ancillary properties to be useful in actual service. These include

sufficient solubility or ease of dispersion, high extraction resistance, and low volatility and sufficient thermal stability under processing and service conditions.

Within the last two decades, a number of chemical structures have been proposed as metal deactivators for polyolefins. These include carboxylic acid amides of aromatic mono- and di-carboxylic acids and *N*-substituted derivatives such as *N,N'*-diphenyloxamide, cyclic amides such as barbituric acid, hydrazones and bishydrazones of aromatic aldehydes such as benzaldehyde and salicylaldehyde or of *o*-hydroxy-arylketones, hydrazides of aliphatic and aromatic mono- and di-carboxylic acids as well as *N*-acylated derivatives thereof, bisacylated hydrazine derivatives, polyhydrazides, and phosphorus acid ester of a thiobisphenol. An index of trade names and suppliers of a few commercial metal deactivators is given in [Appendix A4](#).

Though there are metals other than copper (such as iron, manganese and cobalt) that can accelerate thermal oxidation of polyolefins and related polymers such as EPDM, in practice, however, the inhibition of copper-catalyzed degradation of polyolefins is of paramount importance because of the steadily increasing use of polyolefin insulation over copper conductors. Among polyolefins, polyethylene is still the most common primary insulation material for wire and cable. In the United States, high-density polyethylene and ethylenepropylene copolymers are used in substantial amounts for communications wire insulation.

For stabilization of polyolefins in contact with copper, it is often mandatory to combine a metal deactivator with an antioxidant. Metal deactivators in actual use are essentially *N,N'*-bis-[3-(3',5'-di-*tert*-butyl-4'-hydroxy-phenyl)propionyl]-hydrazine and *N,N'*-dibenzaloxalyldihydrazide. The latter compound requires predispersion in a masterbatch because of its insolubility in polyolefins. This is not needed, however, for the former compound, which at commonly used concentrations is molecularly dispersed in polyolefins after processing. The required additive concentrations range from 0.05 to 0.5% depending on the polymer, the nature of the insulation (solid, cellular), whether the cable is petrolatum filled, and on service conditions.

Increasingly, communication cables are filled with petrolatum to improve waterproofing, whereas the insulation may be solid or cellular. Both trends, namely, petrolatum filling and cellular insulation, exert an influence on the oxidative stability of such cables. Thermal stability of high density polyethylene decreases by about 35% in changing from solid to cellular insulation. Moreover, in contact with petrolatum the stability of solid poly-ethylene decreases by 35% and that of cellular polyethylene decreases by 10–40%. Even in the most adverse instance, i.e., cellular insulation in contact with petrolatum, elevated concentrations of antioxidant and metal deactivator make it possible to achieve a high level of stability.

1.18 Light Stabilizers

Most polymers are affected by exposure to light, particularly the ultraviolet (UV) portion of sun's spectrum between 300 and 400 nm. (Fortunately, the earth's atmosphere filters out most of the light waves shorter than 300 nm.) Light contributes very actively to polymer degradation, especially when oxygen is present, which is a normal situation for most plastic materials. For example, when rubber is exposed to UV radiation at 45°C, it oxidizes three times as fast as in the dark at 70°C. Light and oxygen induce degradation reaction in plastics that may not only discolor them but also exert a detrimental influence on numerous mechanical and physical properties. The inhibition of these degradation reactions is essential or else, the applications of many plastics would be drastically reduced. The inhibition can be achieved through addition of special chemicals, light stabilizers, or UV stabilizers, which are capable of interfering with the physical and chemical processes of light-induced degradation.

Carbon black is used as a stabilizer in a limited number of formulations where color is not a criterion. It not only absorbs light, but it can also react with free-radical species that might be formed. The weathering properties of polyethylene are improved by the incorporation of carbon blacks (at 2%–3% concentration). Weather-resistant wire and cable insulation, pipe for outdoor applications, films for mulching, and water conservation in ponds and canals may be made from polyethylene containing carbon black.

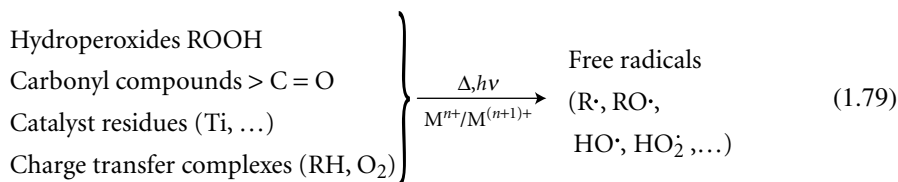
In spite of the fact that carbon black and other pigments may also protect the plastics from the effects of light, we shall consider in the following only those organic and organo-metallic compounds that impart only slight discoloration or no discoloration at all to the plastics to be stabilized.

The most important classes of light stabilizers from a practical point of view are 2-hydroxybenzophenones, 2-hydroxyphenylbenzotriazoles, hindered amines, and organic nickel compounds. In addition, salicylates, *p*-hydroxy-benzoates, resorcinol monobenzoates, cinnamate derivatives, and oxanilides are also used. Light stabilizers are generally used in concentrations between 0.05 and 2%, the upper limit of this range being employed only exceptionally. The sterically hindered amines represent the latest development in the field. They have outperformed the previously available light stabilizer classes in numerous synthetic resins.

1.18.1 Light Stabilizer Classes

The designation of the light stabilizer classes is based on mechanisms of UV stabilization. Free radicals are formed in polymers exposed to light, as a consequence of the excitation of absorbing functionalities in the polymer. This is a function of the energy of the light and of the structure of the polymer molecule. Since in the presence of oxygen, the polymer will simultaneously oxidize (photooxidation), it is often difficult to distinguish the pure photochemical processes from the thermal processes (oxidation), which are then superimposed. Some of the fundamental mechanisms involved have been evaluated [47]. The mechanism developed initially for the thermal oxidation of rubber can be applied to other substrates and also to photooxidation. The scheme shown below illustrates a possible reaction sequence to photooxidation:

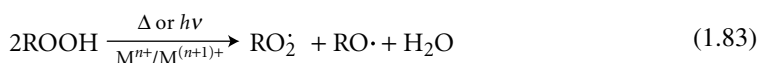
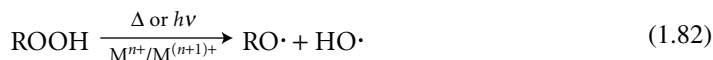
Chain initiation



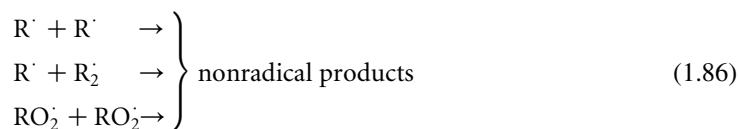
Chain propagation



Chain branching



Chain termination



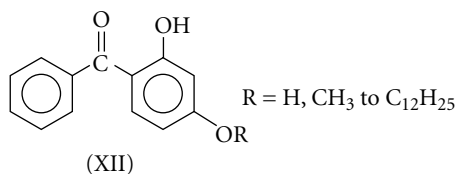
In the light of the above photooxidation scheme there are four possibilities of protection against UV light. These are based on (1) prevention of UV light absorption or reduction of the amount of light absorbed by the chromophores; (2) reduction of the initiation rate through deactivation of the excited states of the chromophoric groups; (3) intervention in the photooxidative degradation process by transformation of hydroperoxides into more stable compounds, without generation of free radicals, before hydroperoxides undergo photolytic cleavage; and (4) scavenging of the free radicals as soon as possible after their formation, either as alkyl radicals or as peroxy radicals.

According to the four possibilities of UV protection mechanism described above, the light stabilizer classes can be designated as (1) UV absorbers, (2) quenchers of excited states, (3) hydroperoxide decomposers, and (4) free radical scavengers. It must be mentioned, however, that this classification is a simplification and that some compounds may be active in more than one way and often do so.

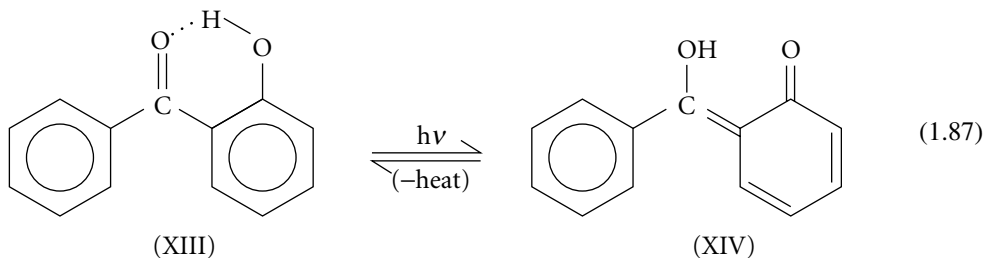
1.18.1.1 UV Absorbers

The protection mechanism of UV absorbers is based essentially on absorption of harmful UV radiation and its dissipation in a manner that does not lead to photosensitization, i.e., conversion to energy corresponding to high wavelengths or dissipation as heat. Besides having a very high absorption themselves, these compounds must be stable to light, i.e., capable of absorbing radiative energy without undergoing decomposition.

Hydroxybenzophenones and hydroxyphenyl benzotriazoles are the most extensively studied UV absorbers. Though the main absorptions of 2-hydroxybenzophenone are situated in the uninteresting wavelength domain around 260 nm, substituents such as hydroxy and alkoxy groups push this absorption towards longer wavelengths, between 300 and 400 nm, and at the same time total absorption in the UV absorbers (XII) are essentially derived from 2,4-dihydroxybenzophenone (X, R=H). Through choice of adequate alkyl group R in the alkoxy groups it is possible to optimize the protective power and the compatibility with the plastics to be stabilized.

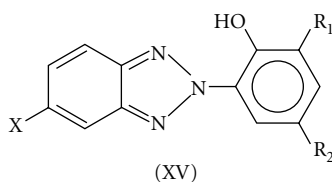


Derivatives of 2-hydroxybenzophenone have highly conjugated structures and a capacity to form intramolecular hydrogen bonds that exert a decisive influence on the spectroscopic and photochemical properties of these compounds. It has been shown with 2-hydroxybenzophenone (XIII) that on exposure to light (XIII) is transformed into enol (XIV), which turns back into its initial form (XIII) on losing thermal energy to the medium (Reaction 1.87):

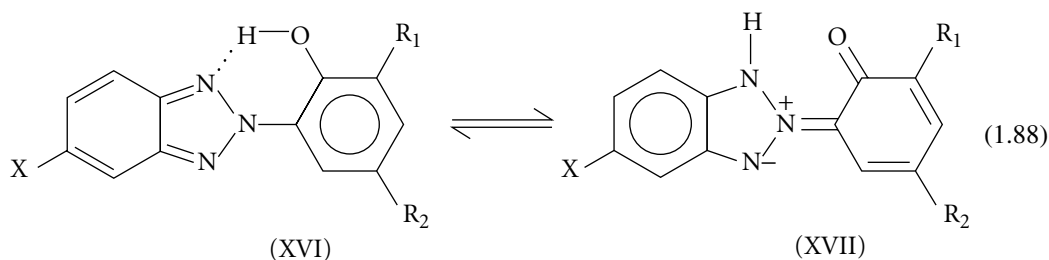


The light energy consumed by the UV absorber corresponds to the quantity of energy needed to break the hydrogen bond. This explanation is supported by the fact that compounds that cannot lead to the formation of intramolecular hydrogen bonds (benzophenone or 2-methoxybenzophenone) do not absorb in the UV wavelength range.

Hydroxyphenyl benzotriazoles have the structure (XV) where X is H or Cl (chlorine shifts the absorption to longer wavelengths), R₁ is H or branched alkyl, and R₂ is CH₃ to C₈H₁₇ linear and branched alkyl (R₁ and R₂ increase the affinity to polymers). Some technically important materials in this class are 2-(2'-hydroxy-5'-methyl-phenyl)-benzotriazole, 2-(2'-hydroxy-3'-5'-di-*tert*-butyl-phenyl)-benzotriazole, and 2-(2'-hydroxy-3',5'-di-*tert*-butyl-phenyl)-5-chlorobenzotriazole. In comparison with 2-hydroxybenzophenones, the 2-(2'-hydroxyphenyl) benzotriazoles have higher molar extinction coefficients and steeper absorption edges towards 400 nm.



The exact mechanism of light absorption by hydrobenzotriazoles is not known. However, the formation of intramolecular hydrogen bond, as in (XVI), and of zwitter ions having a quinoid structure, as in (XVII), may be responsible for the transformation of light radiation energy into chemical modifications:



It may be noted that the tendency to form chelated rings by the creation of hydrogen bonds between hydroxide and carbonyl groups [as in (XIII)] or groups containing nitrogen [as in (XVI)] is a characteristic property of all UV absorbers.

A fundamental disadvantage of UV absorbers is the fact that they need a certain absorption depth (sample thickness) for good protection of a plastic. Therefore, the protection of thin section articles, such as films and fibers, with UV absorbers alone is only moderate.

1.18.1.2 Quenchers

Quenchers (Q) are light stabilizers that are able to take over energy absorbed from light radiation by the chromophores (K) present in a plastic material and thus prevent polymer degradation. The energy absorbed by quenchers can be dissipated either as heat (Reaction 1.91) or as fluorescent or phosphorescent radiation (Reaction 1.92):





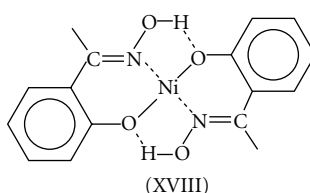
For energy transfer to occur from the excited chromophore K^* (donor) to the quencher Q (acceptor), the latter must have lower energy states than the donor. The transfer can take place by two processes: (1) long-range energy transfer or Förster mechanism and (2) contact, or collisional, or exchange energy transfer.

The Förster mechanism is based on a dipole-dipole interaction and is usually observed in the quenching of excited states. It has been considered as a possible stabilization mechanism for typical UV absorbers with extinction coefficients greater than 10,000. The distance between chromophore and quencher in this process may be as large as 5 or even 10 nm, provided there is a strong overlap between the emission spectrum of the chromophore and the absorption spectrum of the quencher.

However, for an efficient transfer to take place in the contact or exchange energy transfer process, the distance between quencher and chromophore must not exceed 1.5 nm. From calculations based on the assumption of random distribution of both stabilizer and sensitizer in the polymer, it is thus concluded that exchange energy transfer cannot contribute significantly to stabilization. This would not apply, however, if some kind of association between sensitizer and stabilizer takes place (for example, through hydrogen bonding).

Considering the dominant role of hydroperoxides in polyolefin photooxidation [cf. Equation 1.82 and Equation 1.83], quenching of excited $-OOH$ groups would contribute significantly to stabilization. However, since the $-OOH$ excited state is dissociative, i.e., its lifetime is limited to one vibration of the $O-O$ bond, contact energy transfer during this very short time (about 10^{-3} s) appears highly unlikely if the $-OOH$ group is not already associated with the quencher. The quenching action being thus independent of the thickness of the samples, quenchers are specifically useful for the stabilization of thin section articles such as films and fibers.

Metallic complexes that act as excited state quenchers are used to stabilize polymers, mainly polyolefins. They are nickel and cobalt compounds corresponding to the following structure:



Metallic complexes based on Ni, Co, and substituted phenols, thiophenols, dithiocarbamates, or phosphates are used. Typical representatives are nickel-di-butylthiocarbamate, *n*-butylamin-nickel-2,2'-thio-bis-(4-*tert*-octyl-phenolate), nickel-bis-[2,2'-thio-bis-(4-*tert*-octyl-phenolate)] and nickel-(O-ethyl-3,5-di-*tert*-butyl-4-hydroxy-benzyl)-phosphonate. But their use is not as widespread as for other UV absorbers because they tend to be green.

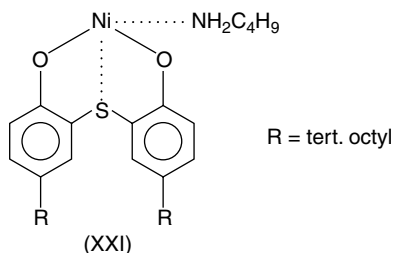
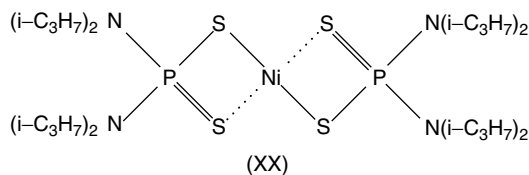
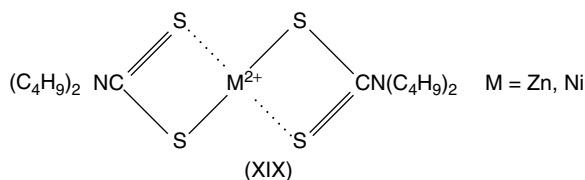
1.18.1.3 Hydroperoxide Decomposers

Since hydroperoxides play a determining role in the photooxidative degradation of polymers, decomposition of hydroperoxides into more stable compounds, before the hydroperoxides undergo photolytic cleavage, would be expected to provide an effective means of UV protection. Metal complexes of sulfur-containing compounds such as dialkyldithiocarbamates (XIX), dialkyldithiophosphates (XX) and thiobisphenolates (XXI) are very efficient hydroperoxide decomposers even if used in almost

catalytic quantities. Besides reducing the hydroperoxide content of pre-oxidized polymer films, they also can act as very efficient UV stabilizers. This explains the fact that an improvement in UV stability is often observed on combining UV absorbers with phosphite or nickel compounds.

1.18.1.4 Free-Radical Scavengers

Besides the absorption of harmful radiation by UV absorbers, the deactivation of excited states by quenchers, and the decomposition of hydroperoxides by some phosphorus and/or sulfur containing compounds, the scavenging of free-radical intermediates is another possibility of photostabilization, analogous to that used for stability against thermooxidative degradation. It has been shown that compounds (XXI), (XXII), (XXIII), and (XXIV) are effective radical scavengers. The radicals generated by hemolytic cleavage of hydroperoxide (Equation 1.93):

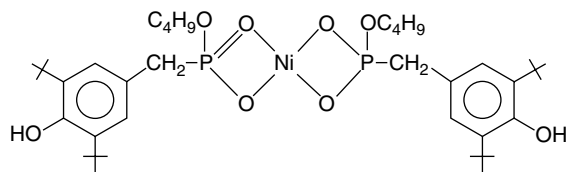


may be removed by reactions, such as



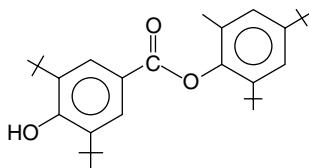
with a radical scavenger InH.

The latest development in the field of light stabilizers for plastics is represented by sterically hindered amine-type light stabilizers (HALS). A typical such compound is bis-(2,2,6,6-tetramethyl-4-piperidyl)-sebacate (XXV). Since it does not absorb any light above 250 nm, it cannot be considered a UV absorber or a quencher of excited states. This has been confirmed in polypropylene through luminescence measurements.

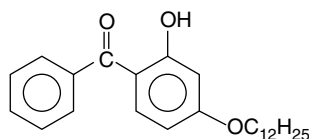


(— = tert butyl)

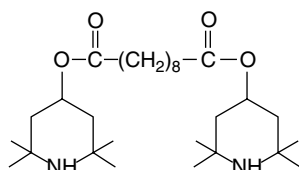
(XXII)



(XXIII)

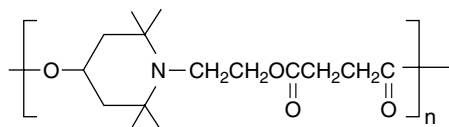


(XXIV)

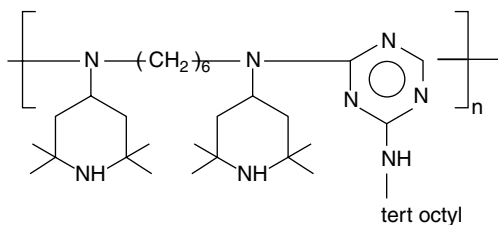


(XXV)

A low-molecular weight HALS such as (XXV), denoted henceforth as HALS-I, has the disadvantage of relative volatility and limited migration and extraction resistance, which are undesirable in special plastics applications (for example, in fine fibers and tapes). For such applications, it is advantageous to use polymeric sterically hindered amines such as poly-(*N*-β-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidyl succinate) represented by (XXVI) and a more complex polymeric hindered amine represented by (XXVII). In later discussions, they will be designated as HALS-II and HALS-III, respectively. Though they do not reach completely the performance of the low-molecular weight HALS-I, they are nevertheless superior to the other common light stabilizers used at several-fold higher concentrations.



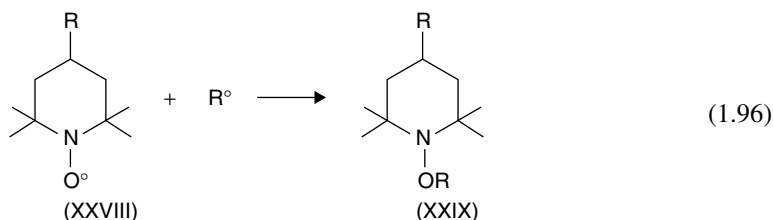
(XXVI)



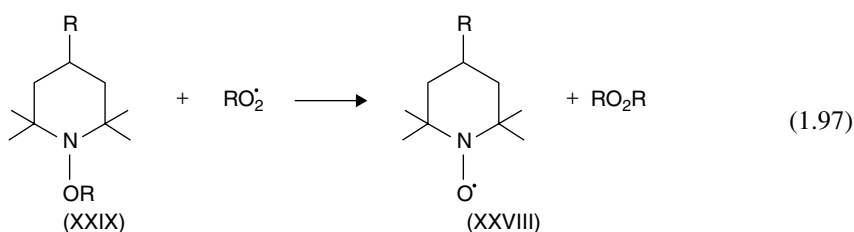
(XXVII)

The protection mechanisms of HALS, known so far mostly from studies with model systems, can be summarized as follows: From ESR measurements it is concluded that, under photooxidative conditions, HALS are converted, at least in part, to the corresponding nitroxyl radicals (XXVIII). The latter, through

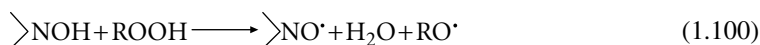
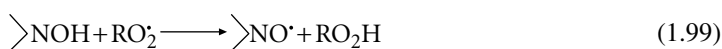
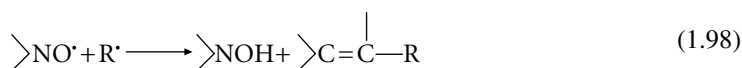
Reaction 1.96, are thought to be the true radical trapping species.



Another explanation of the UV protection mechanism of HALS involves the hydroxylamine ethers (XXIX) formed in Reaction 1.96. There is indirect evidence that (XXIX) can react very quickly with peroxy radicals, thereby regenerating nitroxyl radicals (Reaction 1.97). Reaction 1.96 and Reaction 1.97, which constitute the “Denisov cycle,” result in an overall slowdown of the usual chain oxidation Reaction 1.80 and Reaction 1.81.



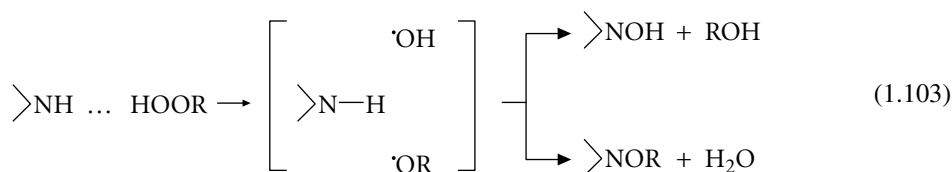
Nitroxyl radicals may also react with polymer radical to form hydroxylamine (Reaction 1.98), and the latter can react with peroxy radicals and hydroperoxides according to Reaction 1.99 and Reaction 1.100:



The formation of associations between HALS and hydroperoxides followed by reaction of these associations with peroxy radicals (Reaction 1.101 and Reaction 1.102) represents another possibility of retarding photooxidation.



The hydroperoxides associated with HALS may undergo photolysis producing hydroxy and alkoxy radicals in close proximity to the amines. The radicals may then abstract a hydrogen atom from the amine and form hydroxylamine and hydroxylamine ethers (Reaction 1.103):



Still other mechanisms have been postulated, e.g., the interaction of HALS with α,β -unsaturated carbonyl compounds and the formation of charge-transfer complex between HALS and peroxy radicals. However, despite extensive publications in the field, a complete knowledge of the process occurring in polymer photooxidation in the presence of HALS is still not available.

1.19 Light Stabilizers for Selected Plastics

In choosing a light stabilizer for a given plastic, several factors, in addition to its protective power, play an important role. In this respect, one may cite physical form (liquid/solid, melting point), thermal stability, possible interaction with other additives and fillers that may eventually lead to discoloration of the substrate, volatility, toxicity (food packaging), and above all, compatibility with the plastics material considered. An additive can be considered as compatible if, during a long period of time, no blooming or turbidity is observed at room temperature and at the elevated temperatures that may be encountered during projected use of the plastic material.

Among the light stabilizer classes available commercially, only a few may be used in a broad range of plastics. Thus, nickel compounds are used almost exclusively in polyolefins, whereas poly(vinyl chloride) is stabilized with UV absorbers only.

A list of trade names and manufacturers of selected light stabilizers is given in [Appendix A5](#).

1.19.1 Polypropylene

For the light stabilization of polypropylene, representatives of the following stabilizer classes are mainly used: 2-(2'-hydroxyphenyl)-benzotriazoles, 2-hydroxy-4-alkoxybenzophenones, nickel-containing light stabilizers, 3,5-di-*tert*-butyl-4-hydroxybenzoates, as well as sterically hindered amines (HALS). Nickel-containing light stabilizers are used exclusively in thin sections, such as films and tapes, whereas all other classes may be used in thin as well as thick sections, though UV absorbers have only limited effectiveness in thin section. Nickel-containing additives are also used as "dyesites" because they allow the dyeing and printing of polypropylene fibers with dyestuffs susceptible to complexation with metals.

1.19.2 Polyethylene

As all polyolefins, polyethylene is sensitive to UV radiation, although less than polypropylene. For outdoor use polyethylene needs special stabilization against UV light. The light stabilizers for polyethylene are in principle the same as for polypropylene. On accelerated weathering, HALS show much better performance in HDPE tapes than UV absorbers, despite the latter being used in much higher concentrations. The comparison between HALS is, however, in favor of the polymeric HALS-III, which has the same performance when added at a concentration of 0.05% as HALS-I and HALS-II at 0.1%.

Among the numerous commercial light stabilizers only a few are suitable for low density polyethylene (LDPE). This is mainly due to the fact that most light stabilizers are not sufficiently compatible at levels of concentration necessary for the required protection and so they bloom more or less rapidly. Initially, UV absorbers of the benzophenone and benzotriazole types were used to protect LDPE materials. With the development of the nickel-quenchers, significant improvement in the light stability of LDPE films has been achieved. For reasons of economy, however, combinations of nickel-quenchers with UV absorbers are mainly used. The service life of LDPE films may be increased by raising the concentrations of light

stabilizers. Additive contents close to 2% may be found in greenhouse films thought to last up to 3 years outdoors.

A further improvement in UV stability of LDPE was expected with the development of HALS. However, LDPE compatibility of HALS available in the early years was insufficient, resulting in relatively poor performance on outdoor weathering. It was only with the development of polymeric HALS that these difficulties were overcome.

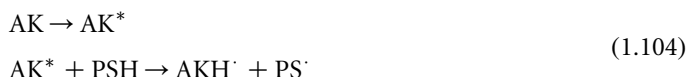
Tests have shown that HALS-II is significantly superior to UV absorbers and Ni-stabilizers so that the same performance can be achieved with much smaller concentrations. However, use of combinations of the polymeric HALS-II with a UV absorber leads to a significant improvement of the efficiency in comparison with the HALS used alone at the same concentration as the combination. A further boost of the performance can be achieved through use of the polymeric HALS-III. For example, the performance of HALS-II can be reached by using HALS-III at about half the concentration. The superiority of HALS-III becomes even more pronounced in films of thickness below 200 μm .

In linear low density polyethylene (LLDPE) also, the polymeric HALS-II and HALS-III show much better performance than other commercial light stabilizers. Blooming is observed with low molecular weight HALS-I, similar to that found with LDPE.

In more polar substances such as ethylene-vinyl acetate copolymers (EVA), the low molecular weight HALS-I can be used. However, in this substrate too, the polymeric HALS-II and HALS-III are significantly superior to the low molecular weight HALS.

1.19.3 Styrenic Polymers

Double bonds are not regarded as the chromophores responsible for initiation of photooxidation in polystyrenes because they absorb below 300 nm. However, peroxide groups in the polymer chain, resulting from co-polymerization of oxygen with styrene, are definitely photolabile. Moreover, oxidation products such as aromatic ketones of acetophenone type, which have been detected by emission spectroscopy, are formed during processing of styrene polymers at high temperatures. Aromatic ketones (AK) in the triplet state are able to abstract hydrogen from polystyrene (PSH) (Reaction 1.104):



This reaction is considered the most important initiation mechanism for styrene photooxidation in the presence of aromatic ketones.

Styrenic plastics such as acrylonitrile/butadiene/styrene graft copolymers (ABS) and impact-resistant polystyrenes are very sensitive towards oxidation, mainly because of their butadiene content. Degradation on weathering starts at the surface and results in rapid loss of mechanical properties such as impact strength.

Because of the lack of efficient light stabilizers, ABS has not been used outdoors on a large scale. However, by combining two light stabilizers with different protection mechanisms, e.g., a UV absorber of the benzotriazole class and the sterically hindered amine HALS-I, it is possible to achieve good stabilization even in ABS. This is a case of synergism in which the UV absorber protects the deeper layers, while HALS-I assures surface protection. At the same time discoloration of the ABS polymer is also reduced significantly. The same holds for polystyrene and styrene-acrylonitrile copolymers (SAN), and the best protection is obtained with HALS/UV absorber combinations. Light stabilization is necessary for articles of these polymers for which UV exposure can be expected (e.g., covers for fluorescent lights).

1.19.4 Poly(Vinyl Chloride)

“Pure” poly(vinyl chloride) (PVC) does not absorb any light above 220 nm. Different functional groups and structural irregularities that may arise during polymerization and processing have thus been

considered as possible initiating chromophores. They include irregularities in the polymer chain as well as hydroperoxides, carbonyl groups, and double bonds.

Thermal stabilizers used in PVC also confer some degree of light stability. Ba/Cd salts and organic tin carboxylates, for example, confer already some UV stability to PVC on outdoor exposure. However, for transparent and translucent PVC articles requiring high UV stability, the light stability conferred by thermal stabilizers is not sufficient. The addition of light stabilizers in such cases is therefore mandatory. So far, UV absorbers yield the best results in practical use. HALS-I has almost no effect.

1.19.5 Polycarbonate

Bisphenol-A polycarbonate (PC) absorbs UV light below 360 nm but its absorption is intense only below 300 nm. Insufficient light stability of PC on outdoor use is manifested by yellowing, which increases rapidly.

Studies indicate that on absorption of UV light, PC undergoes photo-Fries rearrangement, which gives first a phenyl salicylate, and after absorption of a second photon and subsequent rearrangement, it gives 2,2'-dihydroxybenzophenone groups (Figure 1.43). The absorption of these groups reaches into the visible region, and PC yellowing has been essentially attributed to them. In addition to the Fries reaction, the formation of O₂-charge transfer complexes in PC, similar to those found in polyolefins and leading to the formation of hydroperoxides, is considered to contribute significantly to photooxidation in the early stages.

Among the stabilizer classes, only UV absorbers are in use for stabilization of PC. In choosing a UV absorber, intrinsic performance, volatility, adequate thermal stability at the elevated processing temperatures (about 320°C), and effect on initial color of the PC articles should be considered. Benzotriazole, oxanilide, and cinnamate-type UV absorbers are effective photostabilizers for PC with benzotriazoles giving the best performance among the three types.

1.19.6 Polyacrylates

Poly(methyl methacrylate) (PMMA) is highly transparent in the UV region, and thus much more light stable than other thermoplastics. UV absorbers may therefore be used to confer a UV filter effect to PMMA articles. PMMA window panes for solar protection containing 0.05%–0.2% 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole are well-known examples of this application. The rear lights of motor cars, electric signs, and covers for fluorescent lights are some applications for which PMMA is UV-stabilized. The excellent light-stabilizing performance of HALS is also found with PMMA.

1.19.7 Polyacetal

Polyacetal is markedly unstable towards lights because even UV radiation of wavelengths as high as 365 nm may initiate its degradation. Polyacetal cannot therefore be used outdoors if it does not contain any light stabilizers. Even after a short weathering, surface crazes and pronounced chalking are observed.

Carbon black (0.5%–3%) is a good stabilizer for polyacetal when sample color is not important. Other possibilities for stabilization are the use of 2-hydroxybenzophenone and, especially, hydroxyphenylbenzotriazole-type UV absorbers. Stabilization with HALS/UV absorber is superior to that with UV absorber alone.

1.19.8 Polyurethanes

Light stability of polyurethanes depends to a large extent on their chemical structure, and both components (i.e., isocyanate and polyol) have an influence. Polyurethanes based on aliphatic isocyanates and polyester diols show the best light stability if yellowing is considered, whereas polyurethanes based on aromatic isocyanates and polyether diols are worst in this respect.

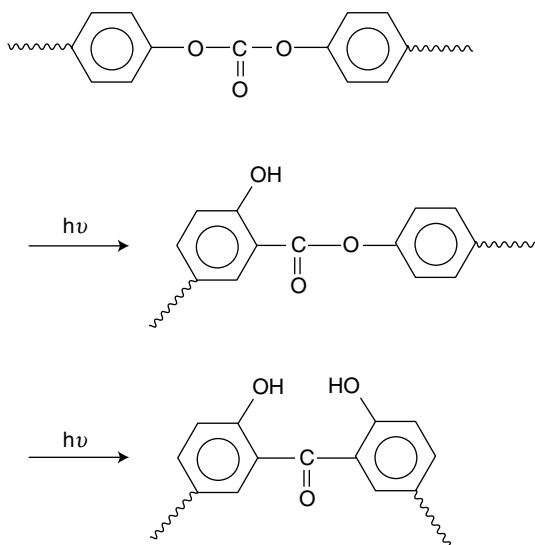


FIGURE 1.43 Photo-Fries rearrangement on polycarbonate.

Light stabilizers are used mainly in the coatings industry (textile coatings, synthetic leather). In addition to some UV absorbers of the 2-(2'-hydroxyphenyl)-benzotriazole type, HALS used alone or in combination with benzotriazoles are especially effective stabilizers.

1.19.9 Polyamides

The absorption of aliphatic polyamides in the short wavelength region of sunlight is attributed largely to the presence of impurities. Direct chain scission at wavelengths below 300 nm and photosensitized oxidation above 300 nm have been considered a long ago as responsible for photooxidation. Antioxidants used in polyamides often confer good light stability as well. However, enhanced performance is obtained with the combination of an antioxidant with a light stabilizer. The sterically hindered amines are significantly superior. For example, molded polyamide samples stabilized with HALS (0.5%) are found to exhibit approximately twice the light stability of the samples stabilized with a phenolic antioxidant (0.5%) or combination of the latter with a UV absorber (0.5%).

1.20 Diffusion and Permeability

There are many instances where diffusion and permeation of a gas, vapor, or liquid through a plastics material is of considerable importance in the processing and usage of the material. For example, dissolution of a polymer in a solvent occurs through diffusion of the solvent molecules into the polymer, which thus swells and eventually disintegrates.

In a plastisol process the gelation of PVC paste, which is a suspension of PVC particles in a plasticizer such as tritolyl phosphate, involves diffusion of the plasticizer into the polymer mass, resulting in a rise of the paste viscosity. Diffusion processes are involved in the production of cellulose acetate film by casting from solution, as casting requires removal of the solvent. Diffusion also plays a part in plastic molding. For example, lubricants in plastics compositions are required to diffuse out of the compound during processing to provide lubrication at the interface of the compound and the mold. Incompatibility with the base polymer is therefore an important criterion in the choice of lubricants in such cases.

Permeability of gases and vapors through a film is an important consideration in many applications of polymers. A high permeability is sometimes desirable. For example, in fruit-packaging applications of plastics film it is desirable to have high permeability of carbon dioxide. On the other hand, for making inner tube and tubeless tires, or in a child's balloon, the polymer used must have low air permeability.

1.20.1 Diffusion

Diffusion occurs as a result of natural processes that tend to equalize the concentration gradient of a given species in a given environment. A quantitative relation between the concentration gradient and the amount of one material transported through another is given by Fick's first law:

$$dm = -D \frac{dc}{dx} A dt \quad (1.105)$$

where dm is the number of grams of the diffusing material crossing area A (cm^2) of the other material in time dt (s). D is the diffusion coefficient (cm^2/s) whose value depends on the diffusing species and the material in which diffusion occurs, and dc/dx is the concentration gradient, where the units of x and c are centimeters and grams per cubic centimeter.

Diffusion in polymers occurs by the molecules of the diffusing species passing through voids and other gaps between the polymer molecules. The diffusion rate will therefore heavily depend on the molecular size of the diffusing species and on the size of the gaps. Thus, if two solvents have similar solubility parameters, the one with smaller molecules will diffuse faster in a polymer. On the other hand, the size of the gaps in the polymer depend to a large extent on the physical state of the polymer—that is, whether it is crystalline, rubbery, or glassy.

Crystalline structures have an ordered arrangement of molecules and a high degree of molecular packing. The crystalline regions in a polymer can thus be considered as almost impermeable, and diffusion can occur only in amorphous regions or through regions of imperfection: hence, the more crystalline the polymer, the greater will be its tendency to resist diffusion. Amorphous polymers, as noted earlier, exist in the rubbery state above the glass transition temperature and in the glassy state below this temperature. In the rubbery state there is an appreciable “free volume” in the polymer mass, and molecular segments also have considerable mobility, which makes it highly probable that a molecular segment will at some stage move out of the way of the diffusing molecule, thus contributing to a faster diffusion rate. In the glassy state, however, the molecular segments cease to have mobility, and there is also a reduction in free volume or voids in the polymer mass, both of which lower the rate of diffusion. Thus, diffusion rates will be highest in rubbery polymers and lowest in crystalline polymers.

1.20.2 Permeability

Permeation of gas, vapor, or liquid through a polymer film consists of three steps: (1) a solution of permeating molecules in the polymer, (2) diffusion through the polymer due to concentration gradient, and (3) emergence of permeating molecules at the outer surface. Permeability is therefore the product of solubility and diffusion; so where the solubility obeys Henry's law one may write

$$P = DS \quad (1.106)$$

where P is the permeability, D is the diffusion coefficient, and S is the solubility coefficient [48].

Hence, factors which contribute to greater solubility and higher diffusivity will also contribute to greater permeability. Thus, a hydrocarbon polymer like polyethylene should be more permeable to hydrocarbons than to liquids of similar molecular size but of different solubility parameter, and smaller hydrocarbons should have higher permeability. The permeabilities of a number of polymers to the common atmospheric gases [49,50], including water vapor, are given in [Table 1.17](#).

It appears that regardless of the film material involved, oxygen permeates about four times as fast as nitrogen, and carbon dioxide about 25 times as fast. The fact that the ratios of the permeabilities for all gases, apart from water vapor, are remarkably constant, provided there is no interaction between the film material and the diffusing gas, leads one to express the permeability as the product of three factors [49]: one determined by the nature of the polymer film, one determined by the nature of the gas, and one accounting for the interaction between the gas and the film; i.e.,

$$P_{i,k} = F_i G_k H_{i,k} \quad (1.107)$$

where $P_{i,k}$ is the permeability for the system polymer i and gas k ; F_i , G_k and $H_{i,k}$ are the factor associated with the film, gas, and interaction respectively. When $H_{i,k} \approx 1$, there is little or no interaction, and as the degree of interaction increases, $H_{i,k}$ becomes larger. With little or no interaction, Equation 1.107 becomes

$$P_{i,k} = F_i G_k \quad (1.108)$$

It then appears that the ratio of the permeability of two gases (k,l) in the same polymer (i) will be the same as the ratio between the two G factors

$$\frac{P_{i,k}}{P_{i,l}} = \frac{G_k}{G_l} \quad (1.109)$$

If the G value of one of the gases, usually nitrogen, is taken as unity, G values of other gases and F values of different polymers can be calculated from Equation 1.109 and Equation 1.108. These values are reliable for gases but not for water vapor. Some F and G values for polymers are given in Table 1.18. Evidently, the F values correspond to the first column of Table 1.17, since G for N_2 is 1. The G values for O_2 and CO_2 represent the averages of P_{O_2}/P_{N_2} and P_{CO_2}/P_{N_2} in columns 5 and 6, respectively.

1.21 Polymer Compounding

In many commercial plastics, the polymer is only one of several constituents, and it is not necessarily the most important one. Such systems are made by polymer compounding—a term used for the mixing of polymer with other ingredients. These other ingredients or supplementary agents are collectively referred to as additives. They may include chemicals to act as plasticizing agents, various types of filling agents, stabilizing agents, antistatic agents, colorants, flame retardants, and other ingredients added to impart certain specific properties to the final product [45,51,52].

The properties of compounded plastics may often be vastly different from those of the base polymers used in them. A typical example is SBR, which is the largest-volume synthetic rubber today. The styrene-butadiene copolymer is a material that does not extrude smoothly, degrades rapidly on exposure to warm air, and has a tensile strength of only about 500 psi (3.4×10^5 N/m²). However, proper compounding changes this polymer to a smooth-processing, heat-stable rubber with a tensile strength of over 3,000 psi (20×10 N/m²). Since all properties cannot be optimized at once, compounders have developed thousands of specialized recipes to optimize one or more of the desirable properties for particular applications (tires, fan belts, girdles, tarpaulins, electrical insulation, etc.).

In SBR the compounding ingredients can be (1) reinforcing fillers, such as carbon black and silica, which improve tensile strength or tear strength; (2) inert fillers and pigments, such as clay, talc, and calcium carbonate, which make the polymer easier to mold or extrude and also lower the cost; (3) plasticizers and extenders, such as mineral oils, fatty acids, and esters; (4) antioxidants, basically amines or phenols, which stop the chain propagation in oxidation; and (5) curatives, such as sulfur for unsaturated polymers and peroxides for saturated polymers, which are essential to form the network of cross-links that ensure elasticity rather than flow.

TABLE 1.17 Permeability Data for Various Polymers

Polymer	Permeability ($P \times 10^{10} \text{ cm}^3/\text{cm}^2/\text{mm}/\text{s}/\text{cm Hg}$)				Ratios (to N_2 Permeability as 1.0)			
	N_2 (30°C)	O_2 (30°C)	CO_2 (30°C)	H_2O (25°C, 90% RH)	$P_{\text{O}_2}/P_{\text{N}_2}$	$P_{\text{CO}_2}/P_{\text{N}_2}$	$P_{\text{H}_2\text{O}}/P_{\text{N}_2}$	Nature of Polymer
Poly(vinylidene chloride) (Saran)	0.0094	0.053	0.29	14	5.6	31	1,400	Crystalline
Polychlorotrifluoro-ethylene	0.03	0.10	0.72	2.9	3.3	24	97	Crystalline
Poly(ethylene terephthalate) (Mylar A)	0.05	0.22	1.53	1,300	4.4	31	26,000	Crystalline
Rubber hydrochloride (Pliofilm ND)	0.08	0.30	1.7	240	3.8	21	3,000	Crystalline
Polyamide (Nylon 6)	0.10	0.38	1.6	7,000	3.8	16	70,000	Crystalline
Poly(vinyl chloride) (unplasticized)	0.40	1.20	10	1,560	3.0	25	3,900	Semicrystalline
Cellulose acetate	2.8	7.8	68	75,000	2.8	24	2,680	Glassy
Polyethylene ($d=0.954, 0.960$)	2.7	10.6	35	130	3.9	13	48	Crystalline
Polyethylene ($d=0.922$)	19	55	352	800	2.9	19	42	Semicrystalline
Polystyrene	2.9	11	88	12,000	3.8	30	4,100	Glassy
Polypropylene ($d=0.910$)	—	23	92	680	—	—	—	Crystalline
Butyl rubber	3.12	13.0	51.8	—	4.1	16.2	—	Rubbery
Polybutadiene	64.5	191	1,380	—	3.0	21.4	—	Rubbery
Natural rubber	80.8	233	1,310	—	2.9	16.2	—	Rubbery

Source: From Stannett, V. T. and Szwarc, M. 1955. *J. Polym. Sci.*, 16, 89 and Paine, F. A. 1962. *J. Roy. Inst. Chem.*, 86, 263.

TABLE 1.18 *F* and *G* Constants for Polymers and Gases

Polymer	<i>F</i>	Gas	<i>G</i>
Poly(vinylidene chloride) (Saran)	0.0094	N ₂	1.0
Poly(chlorotrifluoroethylene)	0.03		
Poly(ethylene terephthalate)	0.05	O ₂	3.8
Rubber hydrochloride (Pliofilm)	0.08	H ₂ S	21.9
Nylon 6	0.1	CO ₂	24.2
Cellulose acetate (+15% plasticizer)	5		
Polyethylene (<i>d</i> =0.922)	19		
Ethyl cellulose (plasticized)	84		
Natural rubber	80.8		
Butyl rubber	3.12		
Nitrile rubber	2.35		
Polychloroprene	11.8		
Polybutadiene	64.5		

Source: From Stannett, V. T. and Szwarc, M. 1955. *J. Polym. Sci.*, 16, 89.

Polymer applications which generally involve extensive compounding are rubbers, thermosets, adhesives, and coatings. Fibers and thermoplastic polymers (with the exception of PVC) are generally not compounded to any significant extend. Fibers, however, involve complex after-treatment processes leading to the final product. PVC, which by itself is a rigid solid, owes much of its versatility in applications to compounding with plasticizers. The plasticize content varies widely with the end use of the product but is typically about 30% by weight.

Of the compounding ingredients, fillers and plasticizers are more important in terms of quantities used. Other additives used in smaller quantities are antioxidants, stabilizers, colorants, flame retardants, etc. The ingredients used as antioxidants and light stabilizers, and their effect have been discussed previously. Fillers, plasticizers and flame retardants are described next.

1.21.1 Fillers

Fillers play a crucial role in the manufacture of plastics. Alone many plastics are virtually useless, but they are converted into highly useful products by combining them with fillers. For example, phenolic and amine resins are almost always used in combination with substances like wood flour, pure cellulose, powdered mica, and asbestos. Glass fiber is used as a filler for fiber-reinforced composites with epoxy or polyester resins.

Another extremely important example is the use of carbon filler for rubber. Rubber would be of little value in modern industry were it not for the fact that the filler carbon greatly enhances its mechanical properties lie tensile strength, stiffness, tear resistance, and abrasion resistance. Enhancement of these properties is called reinforcement, and the fillers which produce the strengthening effect are known as reinforcing fillers. Other fillers may not appreciably increase strength, but they may improve other properties of the polymer, thus, making it easier to mold, which reduces cost.

Fillers used in plastics can be divided into two types: particulate and fibrous. Typical fillers in these two categories and the improvements they bring about are summarized in [Table 1.19](#). In some instances they are added to perform one or more prime functions or to provide special properties. Asbestos, for example, provides high-temperature resistance and improves dimensional stability. Mica improves the electrical and thermal properties of all compounds. Glass fibers produce high strength. Carbon black is the only important reinforcing filler for most elastomers. It also imparts UV resistance and coloring.

Beryllium oxide-filled resins gain high conductivity without loss of electrical properties. Metal particles have been used as fillers for plastics to improve or impart certain properties. Thus, aluminum has been used for applications ranging from making a decorative finish to improving thermal conductivity. Copper particles are used in plastics to provide electrical conductivity. Lead is used because it dampens vibrations, acts as barrier to gamma-radiation, and has high density.

Of the new space-age products used as reinforcing fillers, carbon fibers and boron fibers have the greatest potential for use in high-strength advanced composites. Carbon fibers made by pyrolyzing organic fibers such as rayon and polyacrylonitrile have tensile strengths approaching 3.3×10^5 psi (2.3×10^9 N/m²). Boron fibers made by depositing boron from a BCl₃-H₂ mixture onto tungsten wire have tensile strengths approaching 5×10^5 psi (3.5×10^9 N/m²). The specific strengths and specific moduli of polymer composites made with these fibers are far above those attainable in monolithic structural materials such as high-strength aluminum, steel, and titanium. These composites can thus lead to significant weight savings in actual applications. A relatively recent addition to the high-performance fiber field is the organic polymeric fiber Kevlar-49, developed by Du Pont. It has a higher specific strength than glass, boron, or carbon. Furthermore, Kevlar, a polyamide, is cheap, having one-sixth the price of acrylic-based graphite fibers.

The extensive range of fillers and reinforcing agents used nowadays indicates the importance that these materials have attained. The main difference between inert and reinforcing fillers lies in the fact that modulus of elasticity and stiffness are increased to a greater or less extent by all fillers, including the spherical types such as chalk or glass spheres, whereas tensile strength can be appreciably improved only by a fiber reinforcement. Heat deflection temperature, i.e. stiffness at elevated temperatures, cannot be increased by spherical additives to the same extent as by fiber reinforcement. On the other hand, fillers in flake form, such as talc or mica, likewise produce a marked improvement in the heat deflection temperature but lead to a decrease in tensile strength and to elongation at break. The influences of common fillers on the properties of polyolefins are compared in [Table 1.20](#).

1.22 Plasticizers

Plasticizers are organic substances of low volatility that are added to plastics compounds to improve their flexibility, extensibility, and processability. They increase flow and thermoplasticity of plastic materials by decreasing the viscosity of polymer melts, the glass transition temperature (T_g), the melting temperature (T_m), and the elasticity modulus of finished products [53].

Plasticizers are particularly used for polymers that are in a glassy state at room temperature. These rigid polymers become flexible by strong interactions between plasticizer molecules and chain units, which lower their brittle-tough transition or brittleness temperature (T_b) (the temperature at which a sample breaks when struck) and their T_g value, and extend the temperature range for their rubbery or viscoelastic state behavior (see [Figure 1.19](#)).

Mutual miscibility between plasticizers and polymers is an important criterion from a practical point of view. If a polymer is soluble in a plasticizer at a high concentration of the polymer, the plasticizer is said to be a primary plasticizer. Primary plasticizers should gel the polymer rapidly in the normal processing temperature range and should not exude from the plasticized material. Secondary plasticizers, on the other hand, have lower gelation capacity and limited compatibility with the polymer. In this case, two phases are present after plasticization process—one phase where the polymer is only slightly plasticized, and one phase where it is completely plasticized. Polymers plasticized with secondary plasticizers do not, therefore, deform homogeneously when stressed as compared to primary plasticizers. The deformation appears only in the plasticizer-rich phase and the mechanical properties of the system are poor. Unlike primary plasticizers, secondary plasticizers cannot be used alone and are usually employed in combination with a primary plasticizer.

Plasticizer properties are determined by their chemical structure because they are affected by the polarity and flexibility of molecules. The polarity and flexibility of plasticizer molecules determine their

TABLE 1.19 Some Fillers and Their Effects on Plastics

Properties Improved/Fillers	Chemical Resistance	Heat Resistance	Dimensional Stability	Tensile Strength	Stiffness	Impact Strength	Hardness	Lubricity	Electrical Insulation	Electrical Conductivity	Thermal Conductivity	Moisture Resistance	Processability	Recommend for Use in ^a
Alpha cellulose			+	+					+					S
Alumina	+	+	+											S/P
Aluminum powder										+	+			S
Asbestos	+	+	+		+	+	+		+					S/P
Calcium carbonate		+	+		+		+						+	S/P
Calcium silicate		+	+		+		+							S
Carbon black		+	+		+					+	+		+	S/P
Carbon fiber										+	+			S
Cellulose			+	+	+	+	+							S/P
Cotton (macerated/ chopped fibers)			+	+	+	+	+		+					S
Fibrous glass	+	+	+	+	+	+	+		+			+		S/P
Graphite	+		+	+	+		+	+		+	+			S/P
Jute					+	+								S
Kaolin	+	+	+		+		+	+				+	+	S/P
Kaolin (calcined)	+	+	+		+		+		+			+	+	S/P
Mica	+	+	+		+		+	+	+			+		S/P
Molybdenum disulfide					+		+	+				+	+	P
Nylon (macerated/ chopped fibers)	+	+	+	+	+	+	+	+	+				+	S/P
Acrylic fiber (Orion)	+	+	+	+	+	+	+		+			+	+	S/P
Rayon			+	+	+	+	+		+					S
Silica, amorphous									+			+	+	S/P
TFE-fluorocarbon			+		+		+	+						S/P
Talc	+	+	+		+		+	+	+			+	+	S/P
Wood flour			+	+					+					S

^a P = in thermoplastics only; S = in thermosets only; S/P = in both thermoplastics and thermosets.

TABLE 1.20 Influence of Fillers on the Properties of Polyolefins

Material	Filler Content (%) by wt)	Density (g/cm ³)	Elongation (%)	Tensile Strength (N/mm ²)	Modulus of Elasticity (N/mm ²)	Ball Indentation (N/mm ²)	Heat Deflection Temperature (1.85 N/mm ²) (°C)	Melt Index 190/5 (g/10 min)
Low density								
Polyethylene	—	0.92	500	10	210	16	35	1.7
Chalk	40	1.26	220		900	—	—	0.2
				16				
Glass fiber	30	1.11	65	24	1,200	33	—	1.6
Asbestos	30	1.13	20	20	670	22	—	2.3
Talc		1.14	40	16	600	30	—	1.1
	30							
Mica	30	1.16	46	13	440	27	—	1.2
Glass spheres (< 50 µm)	30	1.11	73	10	290	19	—	2.6
Quartz powder	30	1.14	77	12	400	23	—	2.5
High density								
Polyethylene	—	0.95	> 550	27	1,400	46	50	22
Glass fiber	30	1.16	2	60	7,800	68	108	6
Chalk	30	1.17	9	20	1,900	48	—	18
Wood flour	30	—	6	28	2,100	—	—	—
Kaolin	40	1.24	11	26	2,000	—	—	2.5
Asbestos	40	—	10	30	2,100	—	77	0.7
Polypropylene	—	0.90	620	31	1,600	75	62	1.0
Short glass fiber	30	1.20	5	49	7,500	100	120	6.0
Asbestos	40	1.28	7	45	5,000	84	96	4.0
Talc	40	1.21	11	30	3,100	83	95	3.0
Mica	30	—	—	30	6,900	—	—	—
Chalk	40	1.23	180	25	3,400	63	73	2.5
Wood flour	40	—	8	20	2,200	—	—	—

Source: From Gächter, R. and Müller, H., eds. 1987. *Plastics Additives Handbook*. Hanser Publishers, Munich/New York.

interaction with polymer segments. Plasticizers used in practice contain polar and nonpolar groups, and their ratio determines the miscibility of a plasticizer with a given polymer.

Plasticizers for PVC can be divided into two main groups [51] according to their nonpolar part. The first group consists of plasticizers having polar groups attached to aromatic rings and is termed the polar aromatic group. Plasticizers such as phthalic acid esters and tricresyl phosphate belong to this group. An important characteristic of these substances is the presence of the polarizable aromatic ring. It has been suggested that they behave like dipolar molecules and form a link between chlorine atoms belonging to two polymer chains or to two segments of the same chain, as shown in Figure 1.44a. Plasticizers belonging to this group are introduced easily into the polymer matrix. They are characterized by ability to produce gelation rapidly and have a temperature of polymerplasticizer miscibility that is low enough for practical use. These plasticizers are therefore called solvent-type plasticizers, and their kerosene extraction (bleeding) index is very low. They are, however, not recommended for cold-resistant materials.

The second group consists of plasticizers having polar groups attached to aliphatic chains and is called the polar aliphatic group. Examples are aliphatic alcohols and acid or alkyl esters of phosphoric acid (such as trioctyl phosphate). Their polar groups interact with polar sites on polymer molecules, but since their aliphatic part is rather bulky and flexible other polar sites on the polymer chain may be screened by plasticizer molecules. This reduces the extent of intermolecular interactions between neighboring polymer chains, as shown in Figure 1.44b.

Polar aliphatic plasticizers mix less well with polymers than do polar aromatics and, consequently, may exude (bloom) from the plasticized polymer more easily. Their polymer miscibility temperature is higher than that for the first group. These plasticizers are called oil-type plasticizers, and their kerosene extraction index is high. Their plasticization action is, however, more pronounced than that of polar aromatic plasticizers at the same molar concentration. Moreover, since the aliphatic portions of the molecules retain their flexibility over a large temperature range, these plasticizers give a better elasticity to finished products at low temperature, as compared to polar aromatic plasticizers, and allow the production of better cold-resistant materials. In PVC they also cause less coloration under heat exposure.

In practice plasticizers usually belong to an intermediate group. Mixtures of solvents belonging to the two groups discussed above are used as plasticizers to meet the requirements for applications of the plasticized material.

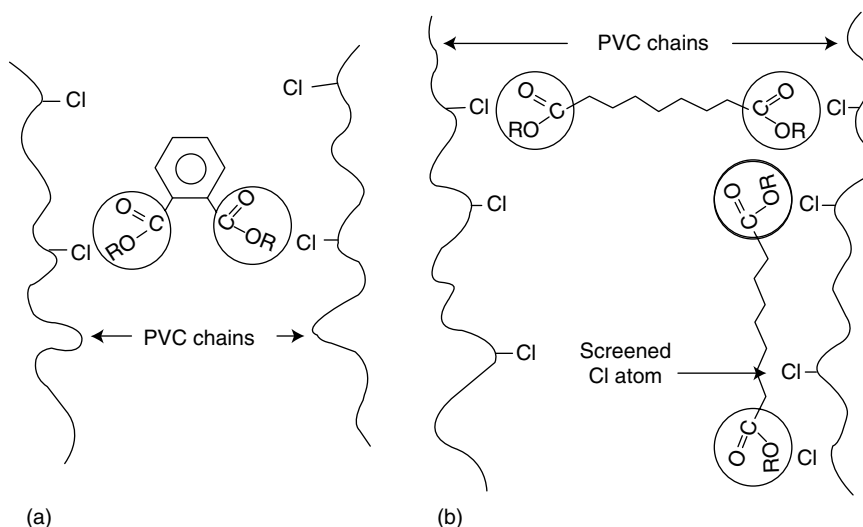


FIGURE 1.44 Action of (a) a polar aromatic plasticizer and (b) a polar aliphatic plasticizer on PVC chains.

Plasticizers can also be divided into groups according to their chemical structure to highlight their special characteristics. Several important plasticizers in each group (with their standard abbreviations) are cited below.

1.22.1 Phthalic Acid Esters

Di(2-ethyl hexyl) phthalate (DOP) and diisooctyl phthalate (DIOP) are largely used for PVC and copolymers of vinyl chloride and vinyl acetate as they have an affinity to these polymers, produce good solvation, and maintain good flexibility of finished products at low temperature. The use of *n*-octyl-*n*-decyl phthalate in the production of plastics materials also allows good flexibility and ductility at low temperature. Diisodecyl phthalate (DDP), octyl decyl phthalate (ODP), and dicapryl phthalate (DCP) have a lower solvency and are therefore used in stable PVC pastes. Butyl octyl phthalate (BOP), butyl decyl phthalate (BDP, and butyl benzyl phthalate (BBP) have a good solvency and are used to adjust melt viscosity and fusion time in the production of high-quality foams. They are highly valued for use in expandable plasticized PVC.

Dibutyl phthalate (DBP) is not convenient for PVC plasticization because of its relatively high volatility. It is a good gelling agent for PVC and vinyl chloride-vinyl acetate copolymer (PVCA) and so is sometimes used as a secondary plasticizer in plasticizer mixers to improve solvation. DBP is mainly used for cellulose-based varnishes and for adhesives. It has a high dissolving capacity for cellulose nitrate (CN).

Dimethyl phthalate (DMP) also has high dissolving capacity for CN. It has good compatibility with cellulose esters and are used in celluloid made from CN and plastic compounds or films made from other cellulosic polymers, cellulose acetate (CA), cellulose acetate-butyrate (CAB), cellulose acetate-propionate (CAP), and cellulose propionate (CP). It is light stable but highly volatile. Diethyl phthalate (DEP) possesses properties similar to DMP and is slightly less volatile.

1.22.2 Phosphoric Acid Esters

Tricresyl phosphate (TCP), trioctyl phosphate, diphenyl 2-ethylhexyl phosphate, and tri(2-ethylhexyl) phosphate (TOP) are used as plasticizers as well as flame retardants. They have a low volatility, resist oil extraction well, and are usually combined with other plasticizers. TCP is a good flame retardant plasticizer for technical PVC, PVAC, NC, and CAB. It is used for PVC articles especially in electrical insulation, but it is not recommended for elastic materials to be used at low temperature. Trioctyl phosphate is a better choice in low temperature applications but it offers a lower resistance to kerosene and oil extraction. Diphenyl 2-ethylhexyl phosphate is a good gelling agent for PVC. It also can be used for materials designed for low temperature application. TOP gels NC, PVCA, and PVC. It has markedly higher volatility than DOP, and it gives plastisols of low viscosity.

1.22.3 Fatty Acid Esters

The esters of aliphatic dicarboxylic acids, mainly adipic, azelaic, and sebacic acid, are used as plasticizers for PVC and PVCA. Di-2-ethylhexyl adipate (DOA), benzyl butyl adipate, di-2-ethylhexyl azelate (DOZ), and di-2-ethyl-hexyl sebacate (DOS) are good examples. They give the polymer outstanding low-temperature resistance and are distinguished by their high light stability. Another characteristic is their low viscosity, which is valuable in the manufacture of PVC plastisols. The solvating action of these esters on PVC at room temperature is weak. This also has a favorable effect on the initial viscosity and storage of plastisols, which is observed even when, for example, plasticizer mixtures of DOP and an aliphatic dicarboxylic ester with DOP contents of up to 80% are used. Such combinations of plasticizers help to improve gelation.

DOS exceeds the low-temperature resistance of all other products in the group. It has the least sensitivity to water and has a relatively low volatility. DOS is used most often because of these properties and because of its high plasticization efficiency.

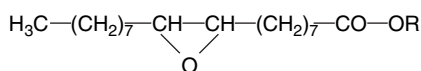
Monoisopropyl citrate, stearyl citrate, triethyl citrate (TEC), butyl and octyl maleates, and fumarates are other important plasticizers for the preparation of stable PC pastes and of low-temperature-resistant PVC products. Triethyl citrate and triethyl acetyl citrate are among the few plasticizers to have good solvency for cellulose acetate. In comparison with diethyl phthalate, with which they are in competition in this application, there are slight but not serious differences in volatility and water sensitivity. The interest in citrate esters is due to a favorable assessment of their physiological properties. They are intended for plastic components used for packaging of food products.

Butyl and octyl maleates, being unsaturated, are used for copolymerization with vinyl chloride, vinyl acetate, and styrene to provide internal plasticization.

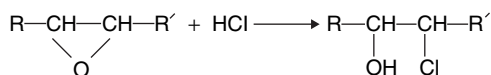
In the production of poly(vinyl butyral), which is used as an adhesive interlayer film between glass plates for safety glass, triethyleneglycol di(2-ethyl) butyrate is an extremely valuable plasticizer that has a proven record of success over many years. It has the required light stability and a plasticizing effect tailored to the requirements of poly(vinyl butyral) that gives the films suitable adhesion to glass ensuring good splinter adhesion over the temperature range from -40 to $+70^{\circ}\text{C}$.

The ethylhexanoic esters of triethylene glycol and polyethylene glycol are good plasticizers for cellulose acetate butyrate (CAB). They, however, have only limited compatibility with poly(vinyl butyral).

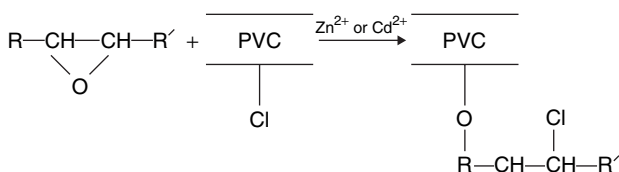
Through the action of peracids on esters of unsaturated fatty acids, oxygen adds to the double bond forming an epoxide group. For example, epoxidized oleates have the following structure:



Since the epoxide group reacts with acids, epoxidized fatty acid esters have become popular as plasticizer for PVC with a good stabilizing effect. Such compounds are not only able to bind hydrogen chloride according to reaction:



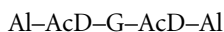
but they are also able to substitute labile chlorine atoms in PVC under the catalytic influence of metal



1.22.4 Polymeric Plasticizers

Polymeric plasticizers can be divided into two main types. Oligomers or polymers of molecular weight ranging from 600 to 8,000 belong to the first group. They include poly(ethylene glycol) and polyesters. High-molecular plasticizers comprise the second group.

Poly(ethylene glycol) is used to plasticize proteins, casein, gelatin, and poly(vinyl alcohol). Polyester plasticizers are condensation products of dicarboxylic acid with simple alcohols corresponding to the following two general formulas:



where Ac, monocarboxylic acid; G, glycol; AcD, dicarboxylic acid; Al, monofunctional alcohol

In practice, esters from adipic, sebacic, and phthalic acid are frequently used as polyester plasticizers. The value of n may vary from 3 to 40 for adipates and from 3 to 35 for sebacates. Polyester plasticizers are seldom used alone. They are used in combination with monomeric plasticizers to reduce the volatility of the mixed solvents. They offer a higher resistance to plasticizer migration and to extract by kerosene, oils, water, and surfactants. Polyester plasticizers are used specially in PVC-based blends and in nitrocellulose varnishes.

Ethylene-vinyl acetate (EVA) polymers (containing 65%–70% by weight of vinyl acetate) are of industrial interest as high-molecular weight plasticizers for PVC, mainly because of their low cost. A polymeric plasticizer PB-3041 available from Du Pont allows the preparation of a highly permanent plasticized PVC formulation. It is believed to be a terpolymer of ethylene, vinyl, acetate, and carbon monoxide. Also, butylene terephthalate-tetrahydrofuran block copolymers, with the trade name of Hytrel (Du Pont), are used as excellent permanent plasticizers of PVC.

1.22.5 Miscellaneous Plasticizers

Hydrocarbons and chlorinated hydrocarbons (chloroparaffins) belong to the secondary plasticizer type.

Aromatic and aliphatic hydrocarbons are used as extenders, particularly in the manufacture of PVC plastisols that must maintain as stable a viscosity as possible for relatively long periods of time (dip and rotational molding). The petroleum industry offers imprecisely defined products with an aliphatic-aromatic structure for use as extenders. They are added to plastisols in small amounts as viscosity regulators. Dibenzyl toluene also serves the same purpose. A disadvantage of this type of extenders is the risk of exudation if excessive quantities are used.

The normal liquid chlorinated paraffins used as plasticizers for PVC have viscosities ranging from 100 to 40,000 MPa.s at 20°C. Products with chlorine contents ranging from 30 to 70% are on the market. Compatibility with PVC increases with increasing chlorine content but the plasticizing effect is reduced. The low viscosity products (chlorine content 30%–40%) are used as secondary plasticizers for PVC. They have a stabilizing effect on viscosity in plastisols. Chlorinated paraffins can be used up to a maximum of 25% of the total plasticizer content of the PVC plastisol without the risk of exudation. As chlorine-containing substances, these plasticizers also have a flame-retarding effect.

At a chlorine content of 50%, chlorinated paraffins are sufficiently compatible with PVC to be used alone, i.e., as primary plasticizers, in semirigid compounds under certain circumstances. Products with extremely good compatibility, however, have low plasticizing action, requiring larger amounts to be used.

Among other plasticizers, *o*- and *p*-toluene-sulfonamides are used to improve the processibility of urea and melamine resins, and cellulose-based adhesives. For the same reason, *N*-ethyl-*o*-toluenesulfonamide and *N*-ethyl-*p*-toluenesulfonamide are used for polyamides, casein, and zein.

Diglycol benzoates are liquid plasticizers rather like benzyl butyl phthalate (BBP) in their plasticizing action in PVC. In the manufacture of PVC floor coverings, the benzoates offer the advantage of a highly soil resistant surface. In this respect, they are even superior to BBP, which itself performs well here.

Pentaerythritol esters can be used instead of phthalic acid esters when low volatility is one of the major factors in the choice of plasticizer for PVC. Pentaerythritol triacrylate can be used to plasticize PVC and to produce cross-links under UV radiation. Such plasticized cross-linked PVC has some application in the cable industry.

Commonly used plasticizers for some polymers beside PVC are listed below:

Cellulosics: Dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), dimethylcyclohexyl phthalate, dimethyl glycol phthalate, trichloroethyl phosphate, cresyldiphenyl phosphate, some glycolates, some sulfonamides.

Poly(vinyl butyrals): Triethyleneglycol di(2-ethyl)butyrate, triethyleneglycol propionate, some adipates, some phosphates.

Polyurethanes: Dibutyl phthalate (DBP), diethyleneglycol dibenzoate (DEGB), and most of the plasticizers used for PVC are preferred for their good plasticization action.

1.23 Antistatic Agents

By virtue of their chemical constitution, most plastics are powerful insulators, a property that makes them useful for many electrical applications. A disadvantage of the insulation property, however, is the accumulation of static electricity, which is not discharged fast enough due to the low surface conductivity of most plastics—a difference between plastics and metals. On plastics and other nonmetallic materials, frictional contact is necessary to generate static charges. On immobile objects, for example, static electricity may build up simply by friction with the ambient air. Electrostatic charges can also be produced on the surfaces of polymeric materials in the course of processing operations such as extrusion, calendaring, and rolling up of plastic sheets or films.

The superficial electrical potential generated by friction may reach values up to a few tens of kilovolts, and this presents serious difficulties for practical applications and to users. Spark formation through heavy charging with subsequent ignition of dust or solvent/air mixtures have been a cause of many destructive explosions. In the service life of plastics products, static charging can give rise to many other troublesome effects, as for example, interference with the sound reproduction of records by dust particles picked up by electrostatic charges, production delays due to clinging of adjacent films or sheets, lump formation during pneumatic transportation, and static build-up on people passing over synthetic fiber carpeting or plastic floor-coverings, with a subsequent “shock” as the charge flows off, usually when the person touches a door handle.

There are many ways to eliminate surface electrostatic, for example, by increasing the humidity or the conductivity of the surrounding atmosphere, or by increasing the electric conductance of materials with the use of electroconducting carbon blacks, powdered metals, or antistatic agents.

Electroconducting carbon blacks are largely utilized to increase the electric conductivity of organic polymers. The electric conductivity of carbon blacks depends, *inter alia*, on the capacity to form branched structures in the polymer matrix, and on the size and size distribution of carbon black particles. The branched and tentacular structures of carbon in the polymer matrix are responsible for the electric conductivity, as is the case for lamp, acetylene, and furnace carbon blacks. The specific resistance of the carbon particles decreases with their size and then increases with further diminution of the size. A wide size distribution is believed to favor the formation of branched structures contributing to greater conductivity.

In spite of the effectiveness of some carbon blacks in reducing surface charges on plastics materials, the use of antistatic agents have increased steadily. The simplest antistatic agent is water. It is adsorbed on the surface of objects exposed to a humid atmosphere, and it forms a thin electroconducting layer with impurities adsorbed from the air. Such a layer is even formed on the surface of hydrophobic plastics, probably because of the existence of a thin layer of dirt.

Antistatic agents commonly used are substances that are added to plastics molding formulations or to the surface of molded articles in order to minimize the accumulation of static electricity. In general terms, antistatic agents can be divided according to the method of application into external and internal agents.

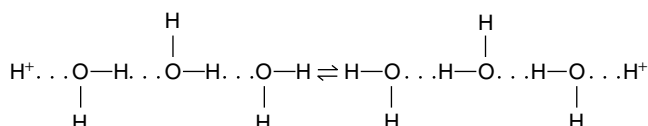
1.23.1 External Antistatic Agents

External antistatic agents are applied to the surface of the molded article from aqueous or alcoholic solution by wetting, spraying, or soaking the plastic object in solution, followed by drying at room temperature or under hot blown air. Their concentration varies between 0.1 and 2% by weight. Almost all

surface active compounds are effective, as well as numerous hygroscopic substances such as glycerin, polyols, and polyglycols, which lack the surface activity feature. The most important external antistatic agents from the practical point of view are quaternary ammonium salts and phosphoric acid derivatives. The advantage of external agents lies in the fact that, in their performance, the properties of compatibility with the polymer and controlled migration in the polymer, which play an important part in the performance of internal antistatic agents described later, are not of any consideration.

It is generally assumed that surface-active molecules accumulate on the surface and are oriented such that the hydrophobic part containing the hydrocarbon chain extends into the plastic, and the hydrophilic part points outwards there it is able to absorb water on the surface. The phase boundary angle between water and plastic is reduced by the surface active antistatic agents thus allowing the absorbed water to be uniformly distributed on the plastic surface. A water film forms on the surface thus increasing the conductivity by means of an ion conduction process. This also explains why surface conductivity, and hence the antistatic action, are found to increase with increasing atmospheric humidity.

For the ion conduction in the surface film, a conductivity mechanism that is similar to protonic conductivity in water has been suggested:



This mechanism is based on a comparison of the conductivities of substances of different chemical structure. For instance, primary amines are efficient as antistatic agents but secondary amines are not. The conductivity of tertiary amines, on the other hand, depends on the nature of *N*-hydroxyalkyl substituents. Among amides, only *N,N*-disubstituted derivatives and mainly those having two hydroxyalkyl substituents are effective. The presence of many OH groups in the molecule makes the efficiency of the antistatic agent less dependent on the humidity. Antistatic agents bearing OH or NH₂ groups are able to associate in chain form via hydrogen bonding and display antistatic activity even at low atmospheric humidity, unlike compounds that are able to form only intramolecular hydrogen bonds.

Many antistatic agents also show hygroscopic properties, thereby intensifying the attraction of water to the surface. At constant atmospheric humidity, a hygroscopic compound attracts more water to the surface and so increases antistatic effectiveness.

1.23.2 Internal Antistatic Agents

Internal antistatic agents are incorporated in the polymer mass as additives, either before or during the molding process. However, to be functional, they must be only partially miscible with the polymer so that they migrate slowly to the surface of the plastics material. Their action therefore appears after a few hours and even a few days after compounding, depending on the mutual miscibility of the agent and the polymer. The concentration of internal antistatic agents in plastics varies from 0.1 to 10% by weight.

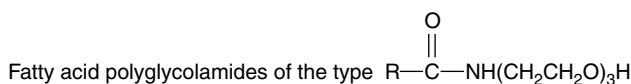
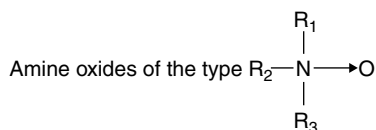
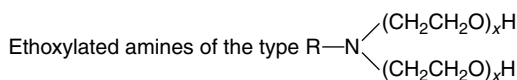
Interfacial antistatic agents are all of interfacially active character, the molecule being composed of a hydrophilic and hydrophobic component. The hydrophobic part confers a certain compatibility with the particular polymer and is responsible for anchoring the molecule on the surface, while the hydrophilic part takes care of the binding and exchange of water on the surface.

1.23.3 Chemical Composition of Antistatic Agents

The selection of an antistatic agent for a given polymer is based on its chemical composition. Accordingly, antistatic agents can be divided in many groups, as presented below.

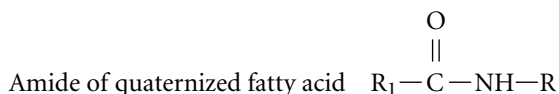
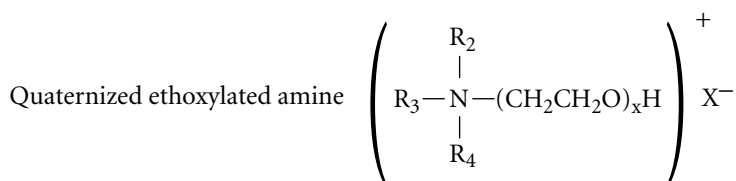
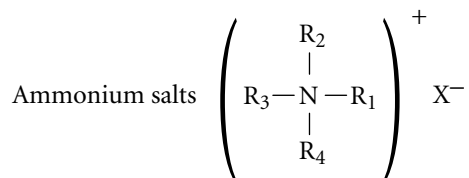
1.23.3.1 Antistatic Agents Containing Nitrogen

Antistatic agents containing nitrogen are mainly amines, amides, and their derivatives, such as amine salts, and addition compounds between oxiranes and aminoalcohols. Pyrrolidone, triazol, and polyamine derivatives also belong to this group. A few representative examples belonging to this group are:

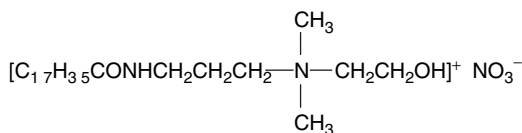


The following two commercial products are typical examples: (1) Alacstat C-2 (Alcolac Chemical Corp., U.S.A.). This is an *N,N*-bis(2-hydroxyethyl)-alkylamine used for polyolefins at 0.1% by weight. (2) Catanac 477 (American Cyanamid Co., U.S.A.). It is *N*-(3-dodecyloxy-2-hydroxypropyl)ethanolamine ($\text{C}_{12}\text{H}_{25}\text{OCH}_2\text{CHOHCH}_2\text{NHCH}_2\text{CH}_2\text{OH}$) used for linear polyethylene (0.15% by weight), for polystyrene (1.5% by weight), and for polypropylene (1% by weight). These compounds are not recommended for PVC.

Other compounds containing nitrogen and used as antistatic agents are quaternary ammonium salts, quaternized amines, quaternized heterocycles obtained from imidazoline and pyridine, and amides of quaternized fatty acids. Some of these compounds can be utilized for PVC for example:

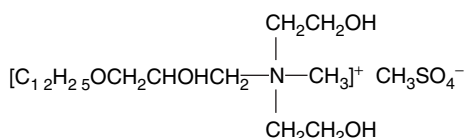


Some typical examples of commercial products are Catanac SN, Catanac 609, Catanac LS, and Catanac SP, all of American Cyanamid Co. Catanac SN is stearamidopropyl-dimethyl- β -hydroxyethylammonium nitrate:



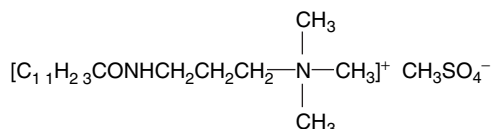
It is available as a 50% by weight solution in a water-isopropanol mixture (pH 4–6). It begins to decompose at 180°C and decomposes very rapidly at 250°C. It is soluble in water, acetone, alcohols, and in a series of polar solvents. It is used as an internal and external antistatic agent for rigid PVC, impact-PS, polyacrylates, ABS terpolymers, paper, and textiles. For applying externally, the concentration of the solution is reduced to 1%–10% by weight. The solution can be applied on the surface of plastic products by rubbing them with a flannel cloth impregnated with the solution. For application as an internal antistatic agent, the commercial higher-concentration solution is directly added to the polymer mixture during the milling or mixing process.

Catanac 609 is *N,N*-bis(2-hydroxyethyl)-*N*-(3'-dodecyloxy-2'-hydroxypropyl) methylammonium methylsulfate:



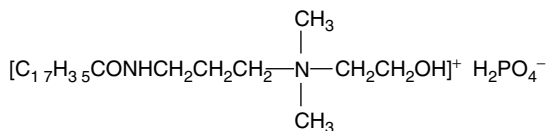
It is supplied mainly as a 50% by weight solution in a water-propanol mixture. It is applied as an external antistatic agent at 2% by weight concentration (pH 4–6) and is recommended for phonograph records and other products made of PVC and its copolymers.

Catanac LS is 3-lauramidopropyl-trimethylammonium methylsulfate:



It exists in a crystalline form with a melting point of 99°C–103°C.

Catanac SP is stearamidopropyl-dimethyl-β-hydroxyethyl-ammonium dihydrogenphosphate:



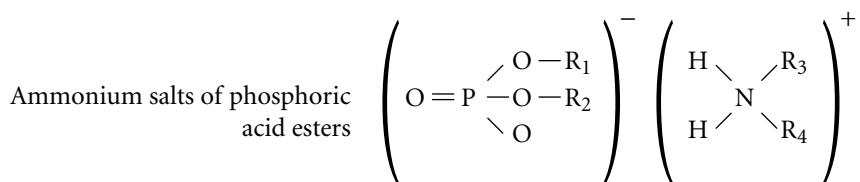
supplied as a 35% by weight solution in a water-isopropanol mixture (pH 6–8). It begins to decompose slightly at 200°C, and at 250°C its decomposition is rapid. It is soluble in water, acetone and alcohols, and is not corrosive to metals even during prolonged contact. Catanac SP can be used as an internal and external antistatic agent at 1%–3% by weight.

1.23.3.2 Antistatic Agents Containing Phosphorus

Antistatic agents that contain phosphorus can be used for all polymers, although they are recommended mainly for PVC with which they also function as plasticizers. They are phosphoric acid derivatives, phosphine oxide, triphosphoric acid derivatives, and substituted phosphoric amides. Typical examples are the following:



Ethoxylated alcohols and phosphoric acid esters $O = P[O(CH_2CH_2O)_x - R]_3$



1.23.3.3 Antistatic Agents Containing Sulfur

Antistatic agents that contain sulfur include compounds such as sulfates, sulfonates, derivatives of aminosulfonic acids, condensation products of ethyleneoxide and sulfonamides, and sulfonates of alkylbenzimidazoles, dithiocarbamides, and sulfides.

Sulfur-containing antistatic agents are recommended mainly for PVC and PS because they do not interfere with heat stabilizers. They are not suitable for PMMA, polyolefins, and polyamides. As examples, there are alkylpolyglycoether sulfates, $RO(CH_2CH_2O)_xSO_3^-Me^+$, which are marketed under the trade name Statexan HA (Bayer).

1.23.3.4 Betaine-Type Antistatic Agents

Betaines are trialkyl derivatives of glycine, which exist as dipolar ions of the formula $R_3^+NCH_2CO_2^-$. Typical examples of betaine-type antistatic agents are stearylbetaine and dodecyldimethyl-ethanesulfobetaine. They are used mainly for polyolefins.

1.23.3.5 Nonionic Antistatic Agents

Nonionic antistatic agents are nonionizable, interfacially active compounds of low polarity. The hydrophilic portion of the molecule is usually represented by hydroxyl groups and the hydrophobic portion by organic groups. This group of antistatic agents includes the following: polyhydroxy derivatives of glycine, sugars, and fatty acids, sometimes modified by addition of oxiranes, most of the products being nontoxic and hygienically acceptable but having low antistatic effects; heavy alcohol derivatives such as alkylpolyglycol ethers, which are recommended for polyolefins and PVC; alkylphenolpolyglycol ethers having good heat stability, which are used mainly for polyolefins; polyglycol ethers ether obtained from the reaction of glycols with oxiranes, which are used for polyolefins; and fatty acid polyglycol esters $RCO_2(CH_2CH_2O)_xH$, which are used for many type of plastics.

Nonionic antistatic agents are supplied for the most parting liquid form or as waxes with a low softening region. The low polarity of this class makes its members ideal internal antistatic agents for polyethylene and polypropylene.

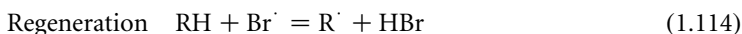
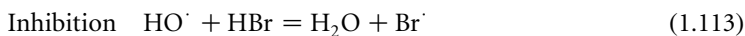
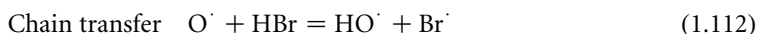
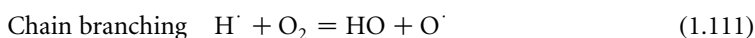
A number of substances that cannot be included in any of the groups above are also good antistatic agents. They are silicone copolymers, organotin derivatives, oxazoline derivatives, organoboron derivatives, and perfluorated surfactants. Some of them show excellent heat stability.

1.24 Flame Retardants

Efforts to develop flame-retarding plastics materials have been focusing on the increasing use of thermoplastics. As a result, flame-retarding formulations are available today for all thermoplastics, which strongly reduce the probability of their burning in the initiating phase of a fire. The possibility of making plastics flame-retardant increases their scope and range of application. (It must be noted, however, that in the case of fire, the effectiveness of flame retardants depends on the period of time and intensity of the fire. Even a product containing the most effective flame-retardants cannot resist a strong and long-lasting fire) [54].

Flame retardants are defined as chemical compounds that modify pyrolysis reactions of polymers or oxidation reactions implied in combustion by slowing them down or by inhibiting them. The combustion of thermo-plastics (see “[Fire Resistant Polymers](#)” in [Chapter 5](#)) is initiated by heating the material up to its decomposition point through heat supplied by radiation, flame, or convection. During combustion, free radicals are formed by pyrolysis and, besides noncombustible gases such as carbon dioxide and water, combustible gases are formed—mainly hydrocarbons, hydrogen, and carbon monoxide. The radicals combine with oxygen and combustible gases in a radical chain reaction, thereby causing heat release and further decomposition of the plastics material. For continued combustion it is necessary to have sufficient oxygen as well as combustible gaseous compounds.

The combustion will be slowed down or inhibited if free radicals, which are evolved by pyrolysis, are blocked. For example, it is presumed that the following reactions take place when thermoplastics containing organobromine compounds as flame retardants are used:



The radical chain reaction is interrupted when the highly reactive HO^\cdot radical, which plays a key role in the combustion process, is replaced by the less reactive Br^\cdot radical (Reaction 1.113). While Equation 1.112 and Equation 1.113 show reactions with HBr (which is released during combustion), experiments have shown that halogen-containing organic compounds may also react as undecomposed molecules.

Flame retardants, in view of the above discussion, can be defined as chemical compounds that modify pyrolysis reactions of polymers or oxidation reactions implied in the combustion by slowing these reactions down or by inhibiting them. In practice, mixtures of flame retardants are often used to combine different types of retardancy effects. In spite of a few thousand references on flame retardants, only a small number of compounds are produced commercially. They are mainly chlorine, bromine, phosphorus, antimony, aluminum, and boron-containing compounds. Trade names and manufactures of some selected flame retardants are given in [Appendix A6](#). Most flame retarding agents may be divided into three groups: (1) halogen compounds, (2) phosphorous compounds, and (3) halogen-antimony synergetic mixtures.

1.24.1 Halogen Compounds

As flame retardants, bromine compounds show superiority over chlorine compounds. For example, in case of combustion of n-heptane/air mixture, the minimum concentrations (in vol. %) found necessary for the extinction of flame are 5.2% for dibromomethane and 17.5% for trichloromethane. The efficiency of halogen-containing agents depends on the strength of the carbon-halogen bond. Thus the relative efficiency of aliphatic halides decreases in the following order:

Aliphatic bromides > aliphatic chlorides = aromatic bromides > aromatic chlorides

It is also known that aromatic bromides have a higher decomposition temperature (250°C–300°C) than aliphatic bromides (200°C–250°C).

Bromine-containing compounds on a weights basis are at least twice as effective as chlorine-containing ones. Because of the smaller quantities of bromine compounds needed, their use hardly influences the mechanical properties of the base resins and reduces markedly the hydrogen halide content of the combustion gases. Aliphatic, cycloaliphatic, as well as aromatic and aromatic-aliphatic bromine compounds are used as flame retardants.

Bromine compounds with exclusively aromatic-bound bromine are produced in large quantities. Occupying the first place is tetrabromobisphenol-A, which is employed as a reactive flame retardant in polycarbonates and epoxy resins. Similarly, tetrabromophthalic anhydride has been used in the production of flame-retarded unsaturated polyester resins.

Brominated diphenyls and brominated diphenylethers—for instance, octabromodiphenyl ether (melting point 200°C–290°C) and decabromodiphenyl ether (melting point 290°C–310°C)—have gained great significance. Possessing excellent heat stability, they are excellent flame retardants for those thermoplastics that have to be processed at high temperatures, such as linear polyesters and ABS.

Aromatic-aliphatic bromine compounds, like the bis(dibromopropyl)-ether of tetrabromobisphenol A, or bromoethylated and aromatic ring-brominated compounds, such as 1,4-bis-(bromoethyl)-tetrabromobenzene, combine the high heat stability of aromatic-bound bromine with the outstanding flame retardancy of aliphatic-bound bromine. They are used mainly as flame retardants for polyolefins, including polyolefin fibers.

Polymeric aromatic bromine compounds, such as poly(tribromostyrene), poly(pentabromobenzyl acrylate) or poly(dibromophenylene oxide) are suitable for application in polyamides, ABS, and polyesters.

Oligomeric bromine-containing ethers on the basis of tetrabromoxylene dihalides and tetrabromobisphenol-A (molecular weight between 3,000 and 7,000) are useful flame retardants for polypropylene, polystyrene, and ABS.

The following cycloaliphatic compounds are suitable as flame retardants in polyolefins: hexabromocyclododecane and bromine-containing Diels-Alder reaction products based on hexachlorocyclopentadiene.

1.24.2 Phosphorus Compounds

Whereas halogen acids, which are released during the combustion of thermoplastics containing organic halogen compounds, interrupt the chain reaction (e.g., Reaction 1.94), the flame-retarding action of phosphorus compounds is not yet fully understood. It is supposed, however, that in case of fire, phosphorus compounds facilitate polymer decomposition, whereby the very stable poly(*meta*-phosphoric acid) formed creates an insulating and protecting surface layer between the polymer and the flame. The phosphoric acid also reacts with the polymer and produces a char layer protecting the surface.

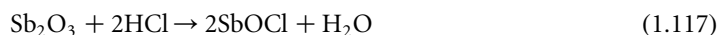
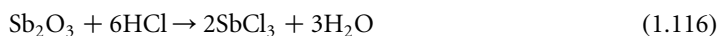
Phosphorus-containing flame retardants may be divided according to the oxidation state of the element into phosphates $[(RO)_3PO]$, phosphites $[(RO)_3P]$, phosphonites $[(RO)_2PR']$, phosphinates $[(RO)R_2'PO]$, phosphines $[R_3P]$, phosphine oxides $[R_3PO]$, and phosphonium salts $[R_4PX]$. The halogenated phosphorus-containing compounds represent a very important group of flame retardants with high efficiency. A few examples are tris-(tribromoneopentyl)-phosphite, tris-(dibromopropyl)-phosphate, tris-(di-bromophenyl)-phosphate, and tris-(tribromophenyl)-phosphate. A similar flame retardancy may also be obtained by the combinations of phosphorus-containing compounds with various halogen derivatives. These combinations are relatively universal in their action.

Phosphorus-containing flame retardants are suitable for polar polymers such as PVC, but for polyolefins their action is not sufficient. In this case they are used together with Sb_2O_3 and with halogenated compounds. Alkyl-substituted aryl phosphates are incorporated into plasticized PVC and modified PPO (Noryl) to a great extent; for other plastics they are less important. Quaternary phosphonium compounds are recommended as flame retardants for ABS and polyolefins.

1.24.3 Halogen–Antimony Synergetic Mixtures

Antimony oxide is an important component of flame retarded thermoplastics containing halogen compounds. Used alone, the flame-retardant effect of antimony oxide is not sufficient, but the effect increases significantly as halogen is added to the system. The basis of this antimony-halogen synergism is probably the formation of volatile flame-retardant SbX_3 (see below), where X is Cl or Br. Antimony-halogen combinations have been widely used in polymer for flame retardation, and the interaction of antimony (mostly as antimony oxide) with halogenated polymers or polymers containing halogenated additives represents the classic case of flame-retardant synergism. Experimental results indicate that the best Sb:X ratio is 1 to 3. More effective are ternary synergetic mixtures such as Sb_2O_3 –pentabromotoluene–chloroparaffin.

The antimony oxide-alkyl (aryl) halide system functions on heating according to the following mechanism (shown for chloride):



Volatile SbCl_3 reduces the formation of radicals in the flame and also affects the oxidation process strongly, thus terminating the combustion. As with phosphorus compounds, it promotes carbonization of the polymer. It is believed that SbOCl and SbCl_3 already function as dehydrogenation agents in the solid phase of the polymer in flame. At 240°C – 280°C , SbOCl is transformed to higher oxychlorides and SbCl_3 , and at temperatures around 500°C the higher antimony oxychlorides are converted back into antimony oxide by releasing again SbCl_3 :



The flame retardation is also attributed to the consumption of thermal energy by these endothermic reactions, to the inhibition reactions in the flame, and to the release of hydrochloric acid directly in the flame. The pigmentation effect of mixtures containing Sb_2O_3 is a disadvantage that limits their use for light-colored and transparent products.

The demands on a flame retardant and thermoplastics formulated with such agents are manifold. The flame retardant should provide a durable flame-retarding effect by the addition of only small quantities of the additive; it should be as cheap as possible and the manner of incorporation should be easy; it should be nontoxic and should not produce fire effluents with increased toxicity; it should not decompose at the processing temperatures; it should not volatilize and smell; and the mechanical, optical, and physical properties of the thermoplastics should be affected as little as possible. It is understandable that these far-ranging demands cannot be satisfied by only one flame retardant and for all thermoplastics with their manifold applications. One is therefore forced to seek the optimum flame retarding formulation for each thermoplastic and the specific application. Examples of typical formulations of several flame-retarded thermoplastics are given in [Appendix A8](#).

1.24.4 Intumescent Flame Retardants

While halogenated compounds are good fire-retardant additives for polyolefins, especially in synergistic combination with antimony trioxide, there are serious disadvantages, such as evolution of toxic gases and corrosive smoke. In the search for halogen-free flame retardants, intumescent flame-retardants (IFRs) have received considerable attention recently, and they have shown particularly good efficiency in the flame retardation of polypropylene (PP) [55]. IFRs that contain ammonium polyphosphate (APP) and pentaerythritol (petol) work mainly through a condensed phase mechanism [56]. APP is most often used as the acid source and petol as a carbon source. These APP-based products also have a low smoke density and do not emit corrosive gases during combustion.

Recently, the synergistic activity of IFRs with heavy metal ions has received wide attention as this can render an IFR more efficient at lower concentrations [57]. It has been found that divalent metal compounds and their derivatives have an excellent synergistic effect when used together with the polyphosphate and petol. Thus, using nickel formate, $\text{Ni}(\text{HCOO})_2$ the limiting oxygen index (LOI) of PP/APP/petol (90: 6.75: 3.25 by wt.) has been found [58] to have the highest value of 30% at 2–3 wt.% $\text{Ni}(\text{HCOO})_2$. It is proposed that during burning, the petol is first phosphorylated by APP, with the release of water and ammonia, while the phosphate ester is pyrolyzed with the formation of double bonds that subsequently cross-link, resulting in a three-dimensional structure.

1.25 Smoke Suppressants

In recent years, the hazards of smoke and toxic gas production by burning have received much greater recognition. Since burning of a large amount of polymer represents a fuel rich combustion, it produces large amounts of toxic carbon monoxide and carbon-rich black smoke, causing death and inhibiting escape from the burning environment. A comparison of smoke production from burning different polymers is given in [Table 1.21](#).

The problem of smoke suppression has not yet been solved satisfactorily, because the demands on flame retardancy and reduced smoke development are principally of antagonistic nature. Most of the developmental work on smoke suppressants has been carried out in the field of PVC. For this polymer, highly dispersed aluminum trihydrate is widely used as a flame retardant and as a smoke suppressant. Antimony trioxide-metal borates (barium borate, calcium borate, and zinc borate) are good smoke reducers. Zinc borate of the formula $2\text{ZnO}:3\text{B}_2\text{O}_3:3.5\text{H}_2\text{O}$ has shown the best effect with regard to reduced flammability and reduced smoke development of PVC. It is possible to reduce smoke development of rigid PVC significantly by adding rather small quantities of molybdc oxide. For example, 2% of molybdc oxide reduces the smoke density to about 35%, but does not decrease the limiting oxygen index value of rigid PVC.

Several methods have been proposed for the determination of the smoke density. Reproducible values are obtained with the laboratory method worked out by the National Bureau of Standards, whereby a specimen of 7.6×7.6 cm is heated by radiation. The smoke density is then measured optically.

1.26 Colorants

A wide variety of inorganic acid organic materials are added to polymers to impart color. For transparent colored plastics materials, oil-soluble dyes or organic pigments (such as phthalocyanines) having small particle size and refractive index near that of the plastic are used. Others, including inorganic pigments, impart opaque color to the plastic. Some of the common colorants for plastics, among many others, are barium sulfate and titanium dioxide (white), ultramarine blues, phthalocyanine blues and greens, chrome green, molybdate organs, chrome yellow, cadmium reds and yellows, quinacridone reds and

TABLE 1.21 Smoke Emission on Burning (NBS Smoke Chamber, Flaming Condition)

Polymer	Maximum Smoke Density (D_{\max})
ABS	800
Poly(vinyl chloride)	520
Polystyrene	475
Polycarbonate	215
Polyamide-imide	169
Polyarylate	109
Polytetrafluoroethylene	95
Polyethersulfone	50
Polyether ether ketone	35

magentas, and carbon black. Flake aluminum is added for a silver metallic appearance, and lead carbonate or mica for pearlescence.

The principal requirements of a colorant are that it have a high covering power-cost ratio and that it withstand processing and service conditions of the plastic. The colorant must not catalyze oxidation of the polymer nor adversely affect its desirable properties. Colorants are normally added to the powered plastic and mixed by tumbling and compounding on a hot roll or in an extruder.

1.27 Antimicrobials

Antimicrobials impart protection against mold, mildew, fungi, and bacterial growth to materials. Without antimicrobials, polymers can experience surface growths, producing allergic reactions, unpleasant odor, staining, embrittlement, and even permanent product failure. The effectiveness of an antimicrobial depends on its ability to migrate to the surface of the product where microbial attack first occurs. Antimicrobials are thus usually carried in plasticizers which are mobile. High mobility, however, can result in leaching of the additives due to weather exposure. The durability of protection is, therefore, determined by a proper balance between migration and leaching.

Of the hundreds of chemicals that are effective as antimicrobials, only a few are used in plastics applications. The most common group of active ingredients consists of 10,16-oxybisphenoxy arsine (OBPA, tradenames: Intercide, Akzo Chemical; Vinyzene, Morton International), 2-*n*-octyl-4-isothiazolin-3-one (tradenames: Micro-Check 11, Ferro Corporation; Vinyzene IT, Morton International), *N*-trichloro-methylthio-4-cyclohexene-1,2-dicarboximide (Captan, tradenames: Vancide 89, R.T. Vanderbilt; Fungitrol C, Hüls America), and *N*-(trichloromethylthio) phthalimide (Flopet, trade name; Fungitrol 11, Huls America). Other antimicrobial active ingredients include amine-neutralized phosphate and zinc 2-pyridinethiol-1-oxide.

OBPA is the most toxic and requires approximately 0.04% active ingredient in the final product. Less toxic active ingredients such as Flopet require a loading of 1.0% to achieve a similar level of protection. Antimicrobials are generally formulated with a carrier into concentrations of 2–5% active ingredient and are available to plastic processors in powder, liquid, or solid-pellet form. The carrier is usually a plasticizer, such as epoxidized soybean oil or diisodecyl phthalate.

Among the antimicrobials, OBPA has broad-spectrum effectiveness against gram-positive and gram-negative bacteria and fungi. Another additive, 2-*n*-octyl-4-isothiazolin-3-one, is a fungicide only and is commonly used to prevent molds in paints. Captan is an agricultural fungicide that has important plastics applications.

The majority of all antimicrobial additives are used in flexible PVC. The remaining portion is used in polyurethane foams and other resins. PVC applications using antimicrobials include flooring, garden hose, pool liners, and wall coverings.

1.28 Toxicity of Plastics

With the expanding use of plastics in all walks of life, including clothing, food packaging, and medical and paramedical applications, attention has been focused on the potential toxic liability of these man-made materials.

Toxic chemicals can enter the body in various ways, particularly by skin absorption, inhalation, and swallowing. Although some chemicals may have an almost universal effect on humans, others may attack few persons. The monomers used in the synthesis of many of the polymers are unsaturated compounds with reactive groups such as vinyl, styrene, acrylic, epoxy, and ethylene imine groups. Such compounds can irritate the mucous membranes of the eyes and respiratory tract and sensitize the skin. They are suspected of including chemical lesions and carcinogenic and mutagenic effects. It was long ago that carcinogenic properties of the monomers vinylchloride and chloroprene were reported, and there may be more trouble ahead in this respect. However, the monomers used in the production of polyester or polyamide resins are usually less reactive and may be expected to be less harmful.

Although many monomers are harmful chemicals, the polymers synthesized from them are usually harmless macromolecules. But then one has to take into account that the polymers may still contain small amounts of residual monomer and catalyst used in the polymerization process. Moreover, polymers are rarely used as such but are compounded, as we saw earlier, with various additives such as plasticizers, stabilizers, curing agents, etc., for processing into plastic good. Being relatively smaller in molecular size, the residual monomer, catalyst residues, and the additives can migrate from the plastic body into the environment. They may eventually migrate into food products packed in plastic containers, or they may interact with the biological substrate when plastics materials are used as parts of tissue and organs implanted into humans. The toxic potential of thermodegradation and combustion products of plastics when these materials are burned, either deliberately or by accident, is also an important consideration in view of the widening use of plastics as structural and decorative lining material in buildings, vehicles, and aircraft.

1.28.1 Plastic Devices in Pharmacy and Medicine

Within the past two decades there has been an increase in the use of a variety of plastic materials in the pharmaceutical, medical, dental, and biochemical engineering fields. Such plastic devices can be classified according to use into six basic groups: (1) collection and administrative devices—e.g., catheters, blood transfusion, sets, dialyzing units, injection devices; (2) storage devices—e.g., bags for blood and blood products, containers for drug products, nutritional products, diagnostic agents; (3) protective and supportive devices—e.g., protective clothes, braces films; (4) implants having contact with mucosal tissue—e.g., dentures, contact lenses, intrauterine devices; (5) permanent implants—e.g., orthopedic implants, heart valves, vascular grafts, artificial organs, and (6) nanomedicines and drug delivery.

The toxic potential of plastic devices becomes more relevant in those applications which involve long periods of contact with the substrate. For short periods of contact, however, a great number of plastic materials manufactured today as medical and paramedical devices will produce little or no irritant response.

With polyethylene, polypropylen, Teflon, Dacron, polycarbonate, and certain types of silicone rubbers, the migration of additives from the material is so small that a biological response cannot be detected. Besides, many of these materials contain additives only in extremely low concentrations, some perhaps having only a stabilizing agent in concentrations of less than 0.1 wt.%. Incidence of tissue response increases when the plastic materials require greater concentrations of various types of additives. It should be stressed, however, that the toxic effects of a material will depend on the intrinsic toxicity of the additives and their ability to migrate from the material to the tissue in contact with it. It is important to know precisely the toxic potential of each of the ingredients in the final polymerized and formulated material to be used in an implantable or storage device.

1.28.1.1 Packing

Many pharmaceutical manufacturers have now taken to packaging their drug product in plastic containers. The plastics used most in these applications are those manufactured from polyethylene and polypropylene, though other materials have also been used. Since both polyethylene and polypropylene contain extremely small amounts of additives (mostly as antioxidants and antistatic agents), the possibility of their release in sufficient concentrations to endanger to patient is negligible.

1.28.1.2 Tubings and Blood Bag Assemblies

Plastic tubings are used for many medical applications, such as catheters, parts of dialysis and administration devices, and other items requiring clear, flexible tubings. The most successful tubing is PVC, which has been plasticized to give it the desired flexibility. Plasticized PVC is also the chief material used in America for making bags for blood and products. In Europe polyethylene and polypropylene have been mainly used. The plasticizers used most for flexible PVC are the esters of phthalic acid; one that is most employed from this group is di-2-ethylhexyl phthalate. Long-term feeding studies have demonstrated the nontoxic nature of the plasticizer under the experimental conditions used. Organotin compounds, which are one of the best groups of stabilizers for vinyl polymers, have been used to stabilize PVC, but, in general, their toxicity has decreased their used in medical applications.

1.28.1.3 Implants

Man-made materials have been used for making implants to save human life. It is possible that these materials, depending on their specific nature and the site of implant, will degrade with long periods of contact and release polymer fragments in the body. These in turn may elicit one or more biological responses, including carcinogenesis. However, no well-substantiated evidence has been reported showing that man-made materials have caused cancer in humans, although the real answer will be available only when these materials have been implanted for periods of time exceeding 20 to 30 years.

Perhaps the most commonly used implantable material is silicone rubber. This material, if properly prepared by the manufacturer, does not cause local toxic response. Various types of epoxy polymers and polyurethane materials also have found one or more medical applications.

1.28.1.4 Adhesives

In most medical and paramedical applications of plastics, the materials used are those already produced by the manufacturers in a polymerized or formulated form. Certain surgical and dental applications, however, require that the material be polymerized or formulated just prior to use. Surgical cements and adhesives, a host of dental filling materials, materials for dentures, cavity liners, and protective coatings for tooth surfaces are in this category.

Cyanoacrylates have become very useful as tissue adhesives in surgical applications, because they polymerize rapidly in contact with moisture and create an extremely tenacious film. Methyl cyanoacrylate, used initially, has now fallen out of favor because of its toxic properties. The butyl and heptyl analogs are, however, quite satisfactory and do not produce objectionable tissue response. They also degrade at a much slower rate than the methyl compound in a biological environment.

1.28.1.5 Dental Materials

Sometimes known as white filling or synthetic porcelain, polymeric dental composites are commonly used as a tooth-colored restorative material, for example, in the fabrication of fillings and veneers, and the cementation of crowns. Dental composites are complex mixtures generally containing an organic resin matrix, reinforcing inorganic filler (such as Sr-glass, 0.7 μm), a silane coupling agent, which connects the filler and the resin matrix, and stabilizers to maximize storage [59]. Composites without the filler and coupling agent are commonly used as sealants, which effectively isolate pits and fissures to help prevent caries.

The dental resins are commonly based on the highly viscous bisphenol A glycidyl methacrylate (abbreviated as bis-GMA, also known as Bowen's monomer after the inventor) have been used for over four decades. Because of its high viscosity (1,369 Pa.s), bis-GMA is blended with diluent, lower molecular weight monomers, to provide a workable matrix resin for composites, for example, bisphenol-A dimethacrylate (bis-DMA), ethylene glycol dimethacrylate (EGDMA), and triethylene glycol dimethacrylate (TEGDMA). Camphorquinone (CQ) is traditionally used as photosensitizer for dental composites. It undergoes a redox reaction with a tertiary amine to produce radicals for free-radical polymerization of the acrylate resin. In a typical procedure, a mixture of bis-GMA and TEGDMA with 1 wt% of CQ and tertiary amine is photopolymerized using visible light device with an intensity of 900 mW/cm². The photopolymerization of the dental resin is fast with most of the reaction taking place within 40 s, causing gelation and vitrification accompanied by shrinkage of about 8%. Shrinkage continues, as also stiffening, during post-polymerization at a much slower rate (see [Table 1.22](#)).

Based on data reported in several studies involving application of sealant to teeth, it appears that low levels of bisphenol A (BPA) may be released from certain sealants, although only during a short time period immediately after application of the sealant. Further, no detectable levels of BPA have been found in blood after application of a sealant that releases low levels of BPA into saliva and the sealant possesses no risk to human health [60].

1.28.1.6 Nanomedicines and Drug Delivery

The term “nano” refers to all molecules and devices/technologies in the size range 1–1,000 nm (a nanometer is 10^{−9} m). Nanomedicine has been defined as “the science and technology of diagnosing, treating, and preventing disease, relieving pain, and preserving and improving human health by using molecular tools and molecular knowledge of the human body.” New drugs and new delivery systems both thus come under the umbrella of nanomedicines. Innovative devices and drug delivery systems are needed to exploit many of the drugs developed from advances in molecular biology, to guide the therapeutic to its correct location of action and ensure that pharmacological activity is maintained for an adequate duration once it is there. In many cases, water soluble polymers are used to carry the active drug into the body without affecting the sites other than the target sites, where the local environment breaks down the polymer releasing the active drug.

“Nanoparticles” are solid colloidal polymeric carriers (less than 1 μm in size) that have received much attention over the recent years due to their ability to control drug release and distribution and due to their biodegradability [62]. Furthermore, these systems have proven their potential to administer peptides or other drugs either by intravenous or oral routes, increasing their bioavailability and protection of the drug against degradation, and reducing the associated adverse effects [63,64].

Most commonly used methods for preparing polymer-based nanoparticles include emulsion evaporation [65], in situ monomer polymerization [66], a method based on the salting out effect [67] and nanoprecipitation [68]. The last named method represents an easy and reproducible technique, which has been widely explored for producing both vesicle and matrix type nanoparticles, also termed nanocapsule and nanosphere, respectively [69]. For the last decade, surfactant-free nanoparticles formation has been investigated by many researchers. Fessi et al. [68] developed surfactant-free nanocapsules of poly(D,L-lactide) (PLA) by the nanoprecipitation technique, using a novel and simple procedure which involved interfacial deposition of a preformed, well-defined and biodegradable polymer following displacement of a semi-polar solvent miscible with water from a lipophilic solution. Nanocapsules of PLA containing indomethacin as a drug model were thus prepared [68]. More recently, poly(lactide-co-glycolide) nanoparticles were prepared by using poly(ethylene glycol)-based block copolymers as substitutes for conventional surfactants [70].

Progress in the development of nano-sized hybrid therapeutics and nano-sized drug delivery systems over the last decade has been remarkable. A growing number of products have already secured regulatory authority approval and, in turn, are supported by a healthy clinical development pipeline. They include products used to treat cancer, hepatitis, muscular sclerosis, and growth hormone deficiency. (See Therapeutics Packaging and Nanomedicines in [Chapter 7](#).)

TABLE 1.22 Young's Modulus, Density, and Shrinkage of Dental Resin Matrix after Photopolymerization

Time after Photopolymerization (s)	Young Modulus (GPa)	Density (g/cm ³)	Shrinkage (%)
0	2.22	1.203	8.02
24	3.27	1.220	9.44
48	3.31	1.222	9.67

Source: From Truffier-Boutry, D., Demonstier-Champagne, S., Devaux, J., Brebuyck, J.-J., Larbanois, P., Mestdagh, M., and Leloup, G. 2005. *Eur. Cell Mater.*, 9, Suppl. 1, 60.

1.28.2 Biodegradable Plastics

The ability to undergo biodegradation producing nontoxic by-products is a useful property for some medical applications. Biodegradable polymers [71] have been formulated for uses such as sutures, vascular grafts, drug delivery devices, and scaffolds for tissue regeneration, artificial skin, orthopedic implants, and others. The polymers commonly known in the medical field for such applications include poly(α -hydroxy esters), poly(ϵ -caprolactone), poly(ortho esters), polyanhydrides, poly(3--hydroxybutyrate), polyphosphazenes, polydioxanones, and polyoxalates (see [Chapter 5](#)).

The homopolymers poly(*L*-lactic acid) (PLLA) and poly(glycolic acid) (PGA) as well as poly(*DL*-lactic-co-glycolic acid) (PLGA) copolymers are poly(α -hydroxy esters). They are biocompatible, biodegradable and are among the few biodegradable polymers with Food and Drug Administration (FDA) approval for human clinical use. PLLA, PLGA copolymers, and PGA are produced by a catalyzed ring—opening polymerization of lactide and/or glycolide. Their degradation in vivo is brought about by simple, non-enzymatic hydrolysis of the ester bond leading, eventually, to lactic acid and/or glycolic acid. These acids are processed through normal metabolic pathways and eliminated from the body ultimately through the respiratory system as carbon dioxide. PGA is a highly crystalline, hydrophilic poly(α -hydroxy ester) and was one of the first synthetic degradable polymers to find application as a biomaterial. One of the first applications of PGA was as a biodegradable suture material. PLLA is one of the strongest known biodegradable polymers and has therefore found many applications in areas, such as orthopedics.

Although organ transplantation has saved many lives, the harsh reality remains that the need for donor organs far outweighs the supply. It is recognized that tissue engineering may provide an alternative to organ transplantation. Tissue engineering involves the creation of natural tissue with the ability to restore missing organ function. This may be achieved either by transplanting cells seeded into a porous material or, in some cases, by relying on ingrowth of tissue and cells into such a material. PGA, PLLA and PLGA copolymers have been used as an artificial scaffold [72] in cell transplantation and organ regeneration (see [Chapter 5](#)).

1.28.3 Oxo-Biodegradable Plastics

Discarded conventional plastics remain in the environment for decades. They block sewers and drains, disfigure the streets, beaches and countryside, and kill wildlife on land, in rivers and oceans. To overcome these problems increasing attention has been paid to the development of degradable plastics: (1) starch-based, biodegradable, (2) aliphatic polyesters, biodegradable, (3) photodegradable, and (4) oxo-biodegradable.

The starch-based plastics do not degrade totally, since only the starch constituent is consumed by microbial activity, and the plastic residues can be harmful to the soil and to birds and insects.

Aliphatic polyesters, described above, are relatively expensive. In the same way as starch, they rely on microbial activity in compost or soil to degrade. Both these products degrade by a process of hydro-degradation.

Photodegradable plastics degrade after prolonged exposure to sunlight, so will not degrade if buried in a landfill, a compost heap, or other dark environment, or if heavily overprinted. Oxo-biodegradable

plastics (Symphony Plastic Technologies, Borehamwood, Herts, U.K.) are a new development. The plastics degrade by a process of oxo-degradation. The technology is based on a small amount (typically 3%) of pro-degradant additive (proprietary) being introduced into the conventional manufacturing process, thereby making the plastic degradable. The degradation, which does not rely on microbes, starts immediately after manufacture and accelerate when exposed to heat, light or stress. The process is irreversible and continues until the whole material reduces to CO₂ and water, leaving no fragments in the soil. The oxo-biodegradable plastics (OBPs) are also consumed by bacteria and fungi after the additive has broken down the molecular structure sufficiently, allowing access to living micro-organisms. So organic wastes in homes, restaurants, hospitals etc. can be put into oxo-biodegradable plastic sacks for disposing straight into the composting plant without emptying the sacks. Even if OBPs were eaten by cow, deer, turtle or other animal whilst still intact, they would degrade even faster due to the temperature and bacteria present in the gut without causing blockage, unlike conventional plastic bags which could kill the animal.

OBPs have an advantage over plastics produced from starch or other agricultural products in that they biodegrade and can be composted but do not need to be buried in a compost heap or landfill in order to degrade. The fact that they can degrade in a normal environment is a significant factor in relation to litter, because a large amount of plastic waste on land and at sea cannot be collected and buried. OBPs can be made transparent and can be used for direct food contact. The length of time OBP takes to degrade totally can be “programmed” at the time of manufacture by varying the amount of additive and can be as little as a few months or as much as a few years.

1.28.4 Toxicity of Plastic Combustion Products

Fires involving plastics produce not only smoke but also other pyrolysis and combustion products. Since most of the polymeric materials contain carbon, carbon monoxide is one of the products generated from the heating and burning of these materials. Depending on the material, the temperature, and the presence or absence of oxygen, other harmful gases may also evolve. These include HCl, HCN, NO₂, SO₂, and fluorinated gases. Presently, various flame-retarding agents are added to plastics to reduce their combustion properties. When heated or subjected to flame, these agents can change the composition of the degradation products and may produce toxic responses not originally anticipated [73].

1.28.5 Toxicity Testing

Ideally, materials for medical and paramedical applications should be tested or evaluated at three level: (1) on the ingredients used to make the basic resin, (2) on the final plastic or elastomeric material, and (3) on the final device. Organizations such as the Association for the Advancement of Medical Instrumentation, the U.S.A. Standard Institute, and the American Society for Testing and Materials (F4 Committee) have developed toxicity testing programs for materials used in medical applications. The American Dental Association has recommended standard procedures for biological evaluation of dental materials [74].

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Fabrication Processes

2.1 Types of Processes

As indicated in [Chapter 1](#), the family of polymers is extraordinarily large and varied. There are, however, some fairly broad and basic approaches that can be followed when designing or fabricating a product out of polymers or, more commonly, polymers compounded with other ingredients. The type of fabrication process to be adopted depends on the properties and characteristics of the polymer and on the shape and form of the final product.

In the broad classification of plastics there are two generally accepted categories: thermoplastic resins and thermosetting resins.

Thermoplastic resins consist of long polymer molecules, each of which may or may not have side chains or groups. The side chains or groups, if present, are not linked to other polymer molecules (i.e., are not cross-linked). Thermoplastic resins, usually obtained as a granular polymer, can therefore be repeatedly melted or solidified by heating or cooling. Heat softens or melts the material so that it can be formed; subsequent cooling then hardens or solidifies the material in the given shape. No chemical change usually takes place during this shaping process.

In thermosetting resins the reactive groups of the molecules form cross-links between the molecules during the fabrication process. The cross-linked or “cured” material cannot be softened by heating. Thermoset materials are usually supplied as a partially polymerized molding compound or as a liquid monomer–polymer mixture. In this uncured condition they can be shaped with or without pressure and polymerized to the cured state with chemicals or heat.

With the progress of technology the demarcation between thermoplastic and thermoset processing has become less distinct. For thermosets processes have been developed which make use of the economic processing characteristics of thermoplastics. For example, cross-linked polyethylene wire coating is made by extruding the thermoplastic polyethylene, which is then cross-linked (either chemically or by irradiation) to form what is actually a thermoset material that cannot be melted again by heating. More recently, modified machinery and molding compositions have become available to provide the economics of thermoplastic processing to thermosetting materials. Injection molding of phenolics and other thermosetting materials are such examples. Nevertheless, it is still a widespread practice in industry to distinguish between thermoplastic and thermosetting resins.

Compression and transfer molding are the most common methods of processing thermosetting plastics. For thermoplastics, the more important processing techniques are extrusion, injection, blow molding, and calendaring; other processes are thermoforming, slush molding, and spinning.

2.2 Tooling for Plastics Processing

Tooling for plastics processing defines the shape of the part. It falls into two major categories, molds and *dies*. A mold is used to form a complete three-dimensional plastic part. The plastics processes that use

molds are compression molding, injection molding, blow molding, thermoforming, and reaction injection molding (RIM). A die, on the other hand, is used to form two of the three dimensions of a plastic part. The third dimension, usually thickness or length, is controlled by other process variables. The plastics processes that use dies are extrusion, pultrusion and thermoforming. Many plastics processes do not differentiate between the terms mold and die. Molds, however, are the most predominant form of plastics tooling.

2.2.1 Types of Mold

The basic types of mold, regardless of whether they are compression, injection, transfer, or even blow molds, are usually classified by the type and number of cavities they have. For example, Figure 2.1 illustrates three mold types: (a) single-cavity, (b) dedicated multiple-cavity, and (c) family multiple-cavity.

Single-cavity mold (Figure 2.1a) represents one of the simplest mold concepts. This design lends itself to low-volume production and to large plastic part designs. The multiple-cavity molds may be of two types. A dedicated multiple-cavity mold (Figure 2.1b) has cavities that produce the same part. This type of mold is very popular because it is easy to balance the plastic flow and establish a controlled process. In a family multiple-cavity mold (Figure 2.1c), each cavity may produce a different part. Historically, family mold designs were avoided because of difficulty in filling uniformly; however, recent advances in mold making and gating technology make family molds appealing. This is the case especially when a processor has a multiple-part assembly and would like to keep inventories balanced.

2.2.2 Types of Dies

Within the plastics industry, the term *die* is most often applied to the processes of extrusion (see [EXTRUSION](#)). Extrusion dies may be categorized by the type of product being produced (e.g., film, sheet, profile, or coextrusion), but they all have some common features as described below.

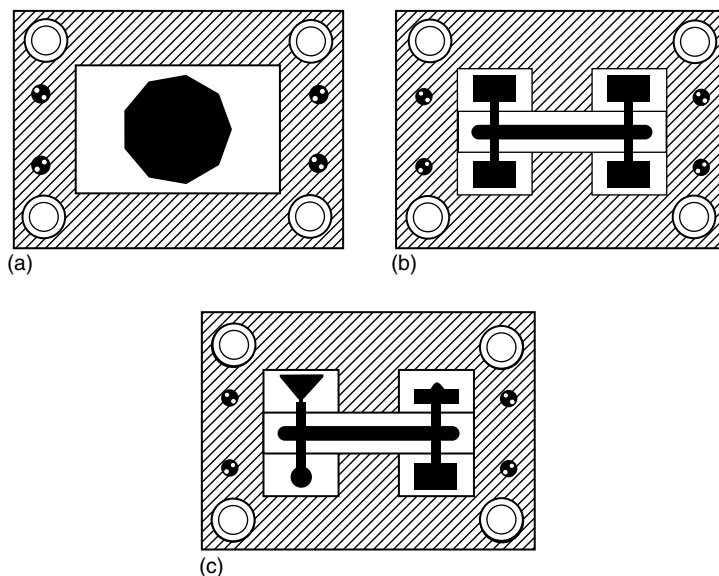


FIGURE 2.1 Three basic types of molds. (a) single-cavity; (b) dedicated multiple-cavity; (c) family multiple-cavity.

1. *Steel.* The extrusion process being continuous, both erosion and corrosion are significant factors. Hence the dies must be made of a high-quality tool steel, hardened so that the areas that contact the plastic material do not erode. Additionally, many dies have a dense, hard chrome plating in the area where plastic melt contacts the die.
2. *Heaters.* Extrusion dies are to be heated in order to maintain a melt flow condition for the plastic material. Most of the heaters are cartridge-type elements that slip fit into the die at particular locations. In addition to the heaters, the dies have to accommodate temperature sensors, such as thermocouples.
3. *Melt Pressure.* Many sophisticated dies are equipped with sensors that monitor melt pressure. This allows the processor to better monitor and control the process.
4. *Parting Line.* Large extrusion dies must be able to separate at the melt flow line for easier fabrication and maintenance. Smaller extrusion dies may not have a parting area, because they can be constructed in one piece.
5. *Die Swell Compensation.* The polymer melt swells when it exits the die, as explained previously. This die swell is a function of the type of plastic material, the melt temperature, the melt pressure, and the die configuration. The die must be compensated for die swell so that the extruded part has the corrected shape and dimensions. Molds and dies for different fabrication processes will be described later in more detail when the processes are discussed.

2.2.3 Tool Design

The design of the tooling to produce a specific plastics part must be considered during the design of the part itself. The tool designer must consider several factors that may affect the fabricated part, such as the plastics material, shrinkage, and process equipment. Additionally, competitive pressures within the plastics industry require the tool designer to consider how to facilitate tool changeovers, optimize tool maintenance, and simplify (or eliminate) secondary operations.

Historically, plastics molds and dies were built by toolmakers who spent their lives learning and perfecting their craft. Today the void created by the waning numbers of these classically trained toolmakers is being filled by the development of numerically controlled (NC) machinery centers, computer-based numerically controlled (CNC) machinery centers, and computer-aided design (CAD) systems. Molds and dies can now be machined on computer-controlled mills, lathes, and electric discharge machines that require understanding of computers and design, rather than years of experience and machining skills. The quality of tool components is now more a function of the equipment than of the toolmaker's skill.

The high costs of molds and the fact that many production molds are built under extreme time constraints leave no room for trial and error. Though prototyping has been widely used to evaluate smaller part designs when circumstances and time allow, prototyping is not always feasible for larger part designs. There are, however, several alternatives to prototyping, e.g., *CAD*, finite-element analysis (FEA), and rapid prototyping. While CAD allows a tool designer to work with a three-dimensional computer model of the tool being designed and to analyze the design, FEA allows the tool to be evaluated (on a computer) for production worthiness. The mold is then fabricated from the computer model, a process called computer-aided manufacturing (CAM).

Rapid prototyping is a relatively new method of producing a plastics part by using a three-dimensional computer drawing. A sophisticated prototyping apparatus interprets the drawing and guides an articulating laser beam across a specific medium such as a photopolymer plastic or laminated paper, the result being a physical representation of the computer-based drawing. Prototyped parts can be produced in less than 24 h, and part designs can be scaled to fit the size of the prototyping equipment. Another trend is the introduction of molds that accept interchangeable modules. Modules take less time to manufacturing, and in turn, cut down on the delivery time and costs. In addition, it usually takes less time to change the module than the entire mold frame.

2.3 Compression Molding

Compression molding is the most common method by which thermosetting plastics are molded [1–3]. In this method the plastic, in the form of powder, pellet, or disc, is dried by heating and then further heated to near the curing temperature; this heated charge is loaded directly into the mold cavity. The temperature of the mold cavity is held at 150°C–200°C, depending on the material. The mold is then partially closed, and the plastic, which is liquefied by the heat and the exerted pressure, flows into the recess of the mold. At this stage the mold is fully closed, and the flow and cure of the plastic are complete. Finally, the mold is opened, and the completely cured molded part is ejected.

Compression-molding equipment consists of a matched mold, a means of heating the plastic and the mold, and some method of exerting force on the mold halves. For severe molding conditions molds are usually made of various grades of tool steel. Most are polished to improve material flow and overall part quality. Brass, mild steel, or plastics are used as mold materials for less severe molding conditions or short-run products.

In compression molding a pressure of 2,250 psi (158 kg/cm²)–3,000 psi (211 kg/cm²) is suitable for phenolic materials. The lower pressure is adequate only for an easy-flow materials and a simple uncomplicated shallow molded shape. For a medium-flow material and where there are average-sized recesses, cores, shapes, and pins in the molding cavity, a pressure of 3,000 psi (211 kg/cm²) or above is required. For molding urea and melamine materials, pressures of approximately one and one-half times that needed for phenolic material are necessary.

The time required to harden thermosetting materials is commonly referred to as the cure time. Depending on the type of molding material, preheating temperature, and the thickness of the molded article, the cure time may range from seconds to several minutes.

In compression molding of thermosets the mold remains hot throughout the entire cycle; as soon as a molded part is ejected, a new charge of molding powder can be introduced. On the other hand, unlike thermosets, thermoplastics must be cooled to harden. So before a molded part is ejected, the entire mold must be cooled, and as a result, the process of compression molding is quite slow with thermoplastics. Compression molding is thus commonly used for thermosetting plastics such as phenolics, urea, melamine, an alkyds; it is not ordinarily used for thermoplastics. However, in special cases, such as when extreme accuracy is needed, thermoplastics are also compression molded. One example is the phonograph records of vinyl and styrene thermoplastics; extreme accuracy is needed for proper sound reproduction. Compression molding is ideal for such products as electrical switch gear and other electrical parts, plastic dinnerware, radio and television cabinets, furniture drawers, buttons, knobs, handles, etc.

Like the molding process itself, compression molding machinery is relatively simple. Most compression presses consist of two platens that close together, applying heat and pressure to the material inside a mold. The majority of the presses are hydraulically operated with plateau ranging in size from 6 in. square to 8 ft square or more. The platens exert pressures ranging from 6 up to 10,000 tons. Virtually all compression molding presses are of vertical design. Most presses having tonnages under 1000 are upward-acting, while most over 1,000 tons act downward. Some presses are built with a shuttle-clamp arrangement that moves the mold out of the clamp section to facilitate setup and part removal.

Compression molds can be divided into hand molds, semiautomatic molds, and automatic molds. The design of any of these molds must allow venting to provide for escape of steam, gas, or air produced during the operation. After the initial application of pressure the usual practice is to open the mold slightly to release the gases. This procedure is known as breathing.

Hand molds are used primarily for experimental runs, for small production items, or for molding articles which, because of complexity of shape, require dismantling of mold sections to release them. Semiautomatic molds consist of units mounted firmly on the top and bottom platens of the press. The operation of the press closes and opens the mold and actuates the ejector system for removal of the molded article. However, an operator must load the molding material, actuate press controls for the molding sequence, and remove the ejected piece from the mold. This method is widely used.

Fully automatic molds are specially designed for adaptation to a completely automatic press. The entire operation cycle, including loading and unloading of the mold, is performed automatically, and all molding operations are accurately controlled. Thermosetting polymers can be molded at rates up to 450 cycles/h. Tooling must be of the highest standard to meet the exacting demands of high-speed production. Automatic molds offer the most economical method for long production runs because labor costs are kept to a minimum.

The three common types of mold designs are open flash, fully positive, and *semipositive*.

2.3.1 Open Flash

In an open flash mold a slight excess of molding powder is loaded into the mold cavity (Figure 2.1a) [4]. On closing the top and bottom platens, the excess material is forced out and flash is formed. The flash blocks the plastic remaining in the cavity and causes the mold plunger to exert pressure on it. Gas or air can be trapped by closing the mold too quickly, and finely powdered material can be splashed out of the mold. However, if closing is done carefully, the open flash mold is a simple one, giving very good results.

Since the only pressure on the material remaining in the flash mold when it is closed results from the high viscosity of the melt which did not allow it to escape, only resins having high melt viscosities can be molded by this process. Since most rubbers have high melt viscosities, the flash mold is widely used for producing gaskets and grommets, tub and flash stoppers, shoe heels, door mats, and many other items.

Because of lower pressure exerted on the plastic in the flash molds, the molded products are usually less dense than when made using other molds. Moreover, because of the excess material loading needed, the process is somewhat wasteful as far as raw materials are concerned. However, the process has the advantage that the molds are cheap, and very slight labor costs are necessary in weighing out the powder.

2.3.2 Fully Positive

In the fully positive molds (Figure 2.2b) no allowance is made for placing excess powder in the cavity [4]. If excess powder is loaded, the mold will not close; an insufficient charge will result in reduced thickness of the molded article. A correctly measured charge must therefore be used with this mold—it is a disadvantage of the positive mold. Another disadvantage is that the gases liberated during the chemical curing reaction are trapped inside and may show as blisters on the molded surface. Excessive wear on the sliding fit surface on the top and bottom forces and the difficulty of ejecting the molding are other reasons for discarding this type of mold. The mold is used on a small scale for molding thermosets, laminated plastics, and certain rubber components.

2.3.3 Semipositive

The semipositive mold (Figure 2.2c and d) combines certain features of the open flash and fully positive molds and makes allowance for excess powder and flash [4]. It is also possible to get both horizontal and vertical flash. Semipositive molds are more expensive to manufacture and maintain than the other types, but they are much better from an applications point of view. Satisfactory operation of semipositive molds is obtained by having clearance (0.025/25 mm of diameter) between the plunger (top force) and the cavity. Moreover, the mold is given a 2–3° taper on each side. This allows the flash to flow on and the entrapped gases to escape along with it, thereby producing a clean, blemish-free mold component.

2.3.4 Process Applicability

Compression molding is most cost-effective when used for short-run parts requiring close tolerances, high-impact strength, and low mold shrinkage. Old as the process may be, new applications continue to

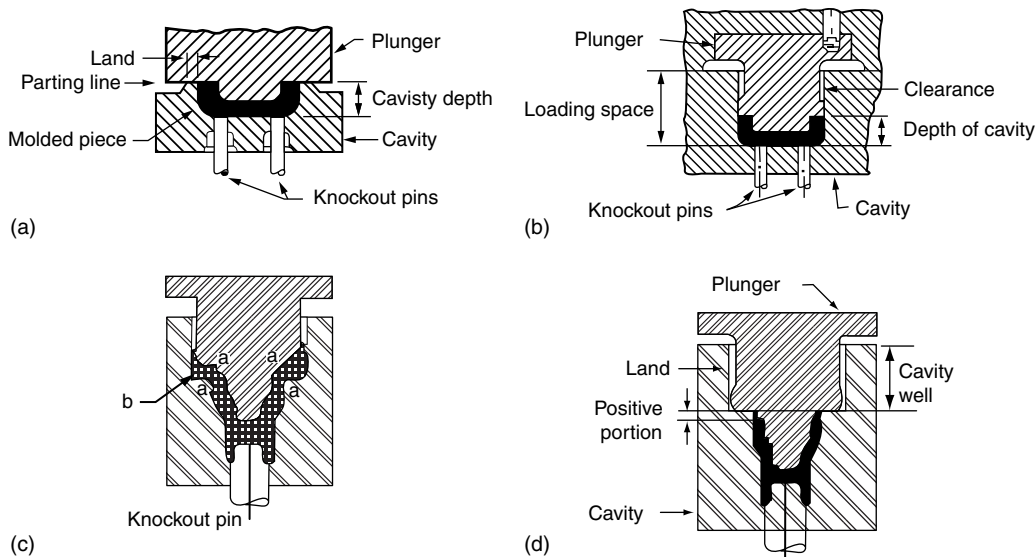


FIGURE 2.2 Compression molds. (a) A simple flash mold. (b) A positive mold. Knockout pins could extend through plunger instead of through cavity. (c) Semi-positive mold as it appears in partly closed position before it becomes positive. Material trapped in area b escapes upward. (d) Semipositive mold in closed position.

evolve compression molding. For example, in the dental and medical fields, orthodontic retainers, and pacemaker casings are now mostly compression molded because of low tool costs. Injection molding tools to produce the same part would cost as much as eight times more. Manufacturers of gaskets and seals who started out with injection-molded products to take advantage of the faster cycle times, are now switching back to compression molding to maintain quality level required for these parts.

The use of compression molding has expanded significantly in recent years due to the development of new materials, reinforced materials in particular. Molding reinforced plastics (RPs) requires two matched dies usually made of inexpensive aluminum, plastics, or steel and used on short runs.

Adding vacuum chambers to compression molding equipment in recent years has reduced the number of defects caused by trapped air or water in the molding compound, resulting in higher-quality finished parts. Another relatively new improvement has been the addition of various forms of automation to the process. For example, robots are used both to install inserts and remove finished parts.

2.4 Transfer Molding

In transfer molding, the thermosetting molding powder is placed in a chamber or pot outside the molding cavity and subjected to heat and pressure to liquefy it [1–6]. When liquid enough to start flowing, the material is forced by the pressure into the molding cavity, either by a direct sprue or through a system of runners and gates. The material sets hard to the cavity shape after a certain time (cure time) has elapsed. When the mold is disassembled, the molded part is pushed out of the mold by ejector pins, which operate automatically.

Figure 2.3 shows the molding cycle of *pot-type transfer molding*, and Figure 2.4 shows *plunger-type transfer molding* (sometime called auxiliary raw transfer molding). The taper of the sprue in pot-type transfer is such that, when the mold is opened, the sprue remains attached to the disc of material left in the pot, known as *cull*, and is thus pulled away from the molded part, whereas the latter is lifted out of the cavity by the ejector pins (Figure 2.3c). In plunger-type transfer molding, on the other hand, the cull and the sprue remains with the molded piece when the mold is opened (Figure 2.4c).

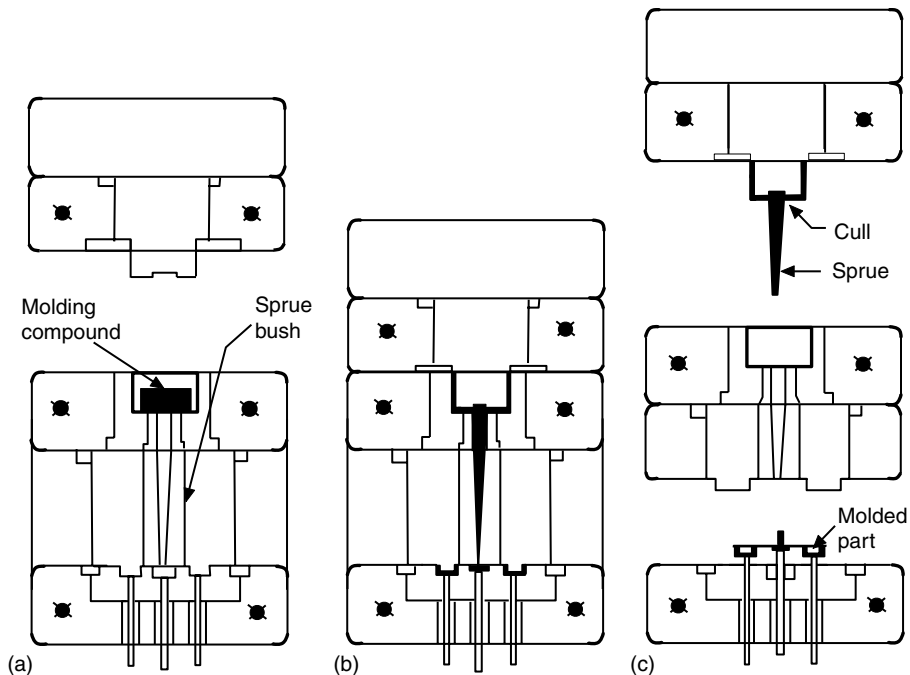


FIGURE 2.3 Molding cycle of a pot-type transfer mold. (a) Molding compound is placed in the transfer pot and then (b) forced under pressure when hot through an orifice and into a closed mold. (c) When the mold opens, the sprue remains with the cull in the pot, and the molded part is lifted out of the cavity by ejector pins. (After Frados, J. ed. 1976. *Plastics Engineering Handbook*, 4th Ed., Van Nostrand Reinhold, New York.)

Another variation of transfer molding is screw transfer molding (Figure 2.5). In this process the molding material is preheated and plasticized in a screw chamber and dropped into the pot of an inverted plunger mold. The preheated molding material is then transferred into the mold cavity by the same method as shown in Figure 2.4. The screw-transfer-molding technique is well suited to fully automatic operation. The optimum temperature of a phenolic mold charge is $240^{\circ}\text{F} \pm 20^{\circ}\text{F}$ ($155^{\circ}\text{C} \pm 11^{\circ}\text{C}$), the same as that for pot-transfer and plunger molding techniques.

For transfer molding, generally pressures of three times the magnitude of those required for compression molding are required. For example, usually a pressure of 9,000 psi (632 kg/cm^2) and upward is required for phenolic molding material (the pressure referred to here is that applied to the powder material in the transfer chamber).

The principle of transferring the liquefied thermosetting material from the transfer chamber into the molding cavity is similar to that of the injection molding of thermoplastics (described later). Therefore the same principle must be employed for working out the maximum area which can be molded—that is, the projected area of the molding multiplied by the pressure generated by the material inside the cavity must be less than the force holding the two halves together. Otherwise, the molding cavity plates will open as the closing force is overcome.

Transfer molding has an advantage over compression molding in that the molding powder is fluid when it enters the mold cavity. The process therefore enables production of intricate parts and molding around thin pins and metal inserts (such as an electrical lug). Thus, by transfer molding, metal inserts can be molded into the component in predetermined positions held by thin pins, which would, however, bend or break under compression-molding conditions. Typical articles made by the transfer molding process are terminal-bloc insulators with many metal inserts and intricate shapes, such as cups and caps for cosmetic bottles.

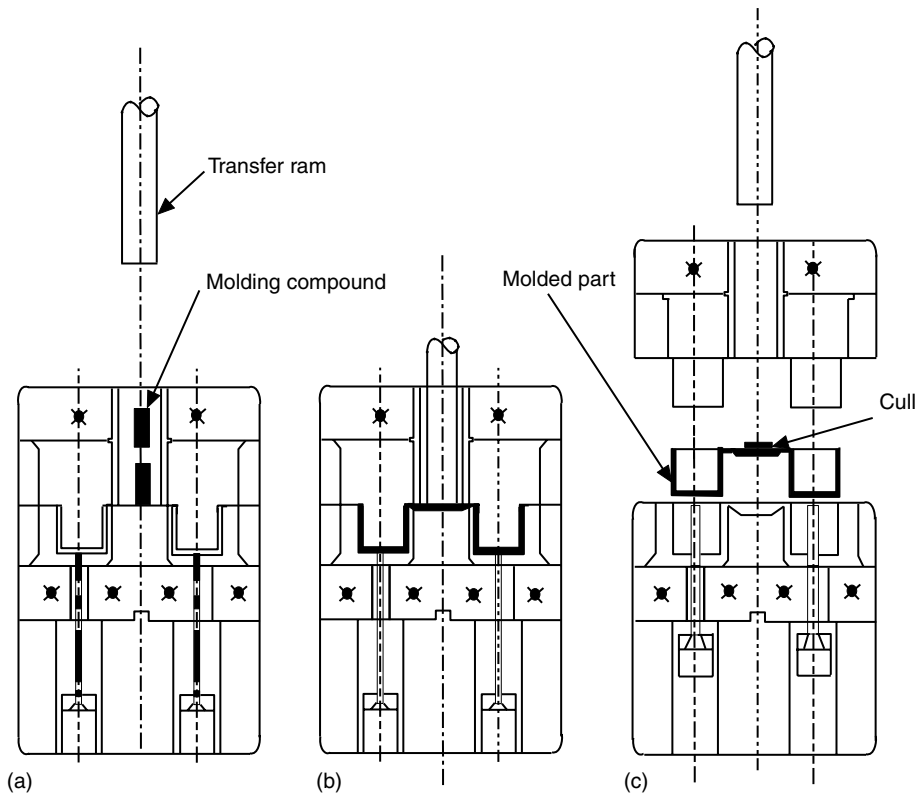


FIGURE 2.4 Molding cycle of a plunger-type transfer mold. (a) An auxiliary ram exerts pressure on the heat-softened material in the pot and (b) forces it into the mold. (c) When the mold is opened, the cull and sprue remain with the molded piece. (After Frados, J. ed. 1976. *Plastics Engineering Handbook*, 4th Ed., Van Nostrand Reinhold, New York.)

2.4.1 Ejection of Molding

Ejection of a molded plastic article from a mold can be achieved by using ejector pins, sleeves, or stripper plates. Ejector pins are the most commonly used method because they can be easily fitted and replaced. The ejector pins must be located in position where they will eject the article efficiently without causing distortion of the part. They are worked by a common ejector plate or a bar located under the mold, and operated by a central hydraulic ejector ram. The ejector pins are fitted either to the bottom force or to the top force depending on whether it is necessary for the molding to remain in the bottom half of the female part or on the top half of the male part of the tool. The pins are usually constructed of a hardened steel to avoid wear.

2.4.2 Heating System

Heating is extremely important in plastics molding operations because the tool and auxiliary parts must be heated to the required temperature, depending on the powder being molded, and the temperature must be maintained throughout the molding cycle. The molds are heated by steam, hot waters, and induction heaters. Steam heating is preferred for compression and transfer molding, although electricity is also used because it is cleaner and has low installation costs. The main disadvantage of the latter method is that the heating is not fully even, and there is tendency to form hot spots.

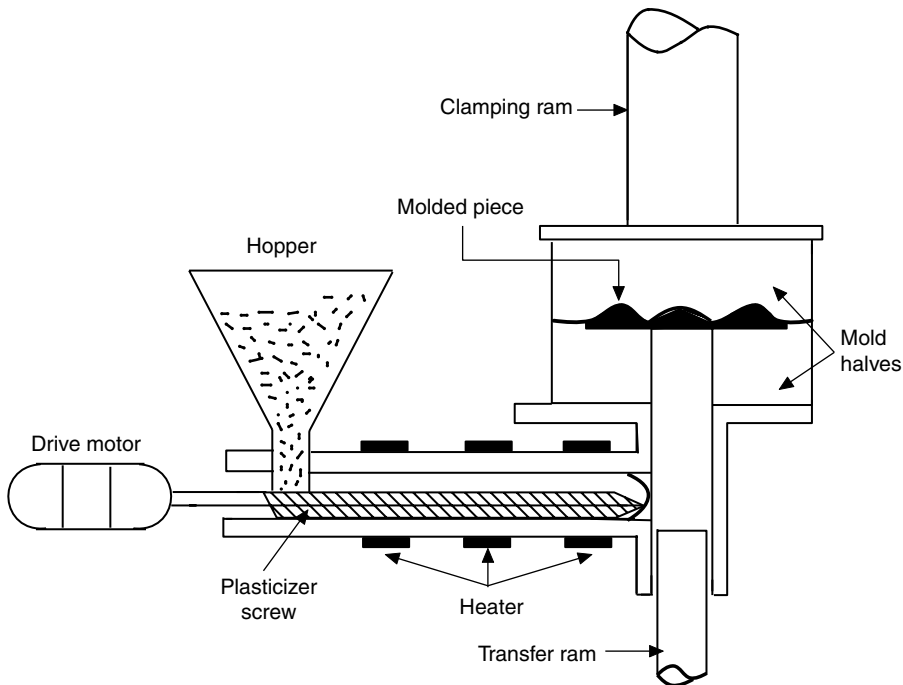


FIGURE 2.5 Drawing of a screw-transfer molding machine. (After Frados, J. ed. 1976. *Plastics Engineering Handbook*, 4th Ed., Van Nostrand Reinhold, New York.)

2.4.3 Types of Presses

Presses used for compression and transfer molding of thermosets can be of many shapes and designs, but they can be broadly classified as hand, mechanical, or hydraulic types. Hand presses have relatively lower capacity, ranging from 10 to 100 tons, whereas hydraulic presses have considerably higher capacity (500 tons). Hydraulic presses may be of the upstroke or downstroke varieties. In the simple upstroke press, pressure can be applied fairly quickly, but the return is slow. In the downstroke press fitted with a prefilling tank, this disadvantage of the upstroke press is removed, and a higher pressure is maintained by prefilling with liquid from a tank.

The basic principles of hydraulics are used in the presses. Water or oil is used as the main fluid. Water is cheap but rusts moving parts. Oil is more expensive but it does not corrode and it does lubricate moving parts. The main disadvantage of oil is that it tends to form sludge due to oxidation with air.

The drive for the presses is provided by single pumps or by central pumping stations, and accumulators are used for storing energy to meet instantaneous pressure demand in excess of the pump delivery. The usual accumulator consists of a single-acting plunger working in a cylinder. The two main types of accumulators used are the weight-loaded type and the air-loaded type. The weight-loaded type is heavy and therefore not very portable. There is also an initial pressure surge on opening the valve. The pressure-surge problem is overcome in the air- or gas (nitrogen)-loaded accumulator. This type is more portable but suffers a small pressure loss during the molding cycle.

2.4.4 Preheating

To cut down cycle times and to improve the finished product of compression molding and transfer molding, the processes of preheating and performing are commonly used. With preheating, relatively thick sections can be molded without porosity. Other advantages of the technique include improved flow of resin, lower molding pressures, reduced mold shrinkage, and reduced flash.

Preheating methods are convection, infrared, radio frequency, and steam. Thermostatically controlled gas or electrically heated ovens are inexpensive methods of heating. The quickest, and possibly the most efficient, method is radio-frequency heating, but it is also the most expensive. Preheaters are located adjacent to the molding press and are manually operated for each cycle.

2.4.5 Preforming

Preforming refers to the process of compressing the molding powder into the shape of the mold before placing it in the mold or to pelleting, which consists of compacting the molding powder into pellets of uniform size and approximately known weight. Preforming has many advantages, which include avoiding waste, reduction in bulk factor, rapid loading of charge, and less pressure than uncompacted material. Preformers are basically compacting presses. These presses may be mechanical, hydraulic, pneumatic, or rotary cam machines.

2.4.6 Flash Removal

Although mold design takes into consideration the fact that flash must be reduced to a minimum, it still occurs to some extent on the molded parts. It is thus necessary to remove the flash subsequent to molding. This removal is most often accomplished with tumbling machines. These machines tumble molded parts against each other to break off the flash. The simplest tumbling machines are merely wire baskets driven by an electric motor with a pulley belt. In more elaborate machines blasting of molded parts is also performed during the tumbling operation.

2.5 Injection Molding of Thermoplastics

Injection molding is the most important molding method for thermoplastics [7–9]. It is based on the ability of thermoplastic materials to be softened by heat and to harden when cooled. The process thus consists essentially of softening the material in a heated cylinder and injecting it under pressure into the mold cavity, where it hardens by cooling. Each step is carried out in a separate zone of the same apparatus in the cyclic operation.

A diagram of a typical injection-molding machine is shown in [Figure 2.6](#). Granular material (the plastic resin) falls from the hopper into the barrel when the plunger is withdrawn. The plunger then pushes the material into the heating zone, where it is heated and softened (plasticized or plasticated). Rapid heating takes place due to spreading of the polymer into a thin film around a torpedo. The already molten polymer displaced by this new material is pushed forward through the nozzle, which is in intimate contact with the mold. The molten polymer flows through the sprue opening in the die, down the runner, past the gate, and into the mold cavity. The mold is held tightly closed by the clamping action of the press platen. The molten polymer is thus forced into all parts of the mold cavities, giving a perfect reproduction of the mold.

The material in the mold must be cooled under pressure below T_m or T_g before the mold is opened and the molded part is ejected. The plunger is then withdrawn, a fresh charge of material drops down, the mold is closed under a locking force, and the entire cycle is repeated. Mold pressures of 8,000–40,000 psi (562–2,812 kg/cm²) and cycle times as low as 15 sec are achieved on some machines.

Note that the feed mechanism of the injection molding machine is activated by the plunger stroke. The function of the torpedo in the heating zone is to spread the polymer melt into thin film in close contact with the heated cylinder walls. The fins, which keep the torpedo centered, also conduct heat from the cylinder walls to the torpedo, although in some machines the torpedo is heated separately.

Injection-molding machines are rated by their capacity to mold polystyrene in a single shot. Thus a 2-oz machine can melt and push 2 oz of general-purpose polystyrene into a mold in one shot. This capacity is determined by a number of factors such as plunger diameter, plunger travel, and heating capacity.

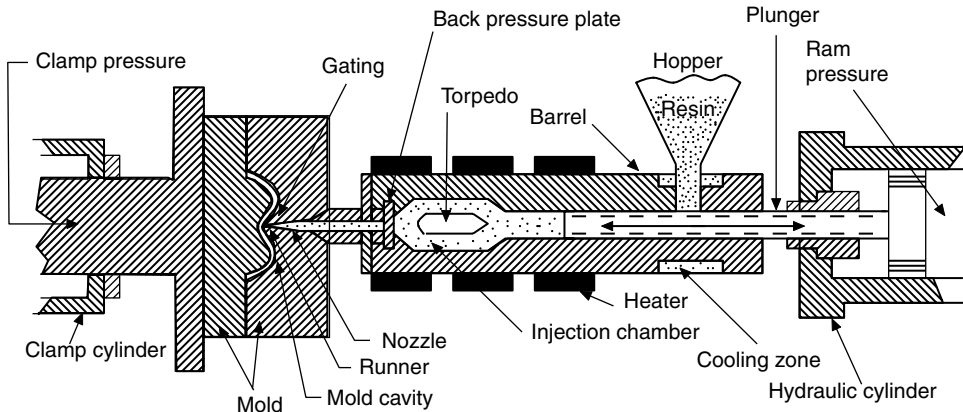


FIGURE 2.6 Cross-section of a typical plunger injection-molding machine. (After Lukov, L. J. 1963. *SPE J.*, 13(10), 1057.)

The main component of an injection-molding machine are (1) the injection unit which melts the molding material and forces it into the mold; (2) the clamping unit which opens the mold and closes it under pressure; (3) the mold used; and (4) the machine controls.

2.5.1 Types of Injection Units

Injection-molding machines are known by the type of injection unit used in them. The oldest type is the single-stage plunger unit (Figure 2.6) described above. As the plastic industry developed, another type of plunger machine appeared, known as a two-stage plunger (Figure 2.7a). It has two plunger units set one on top of the other. The upper one, also known as a preplasticizer, plasticizes the molding material and feeds it to the cylinder containing the second plunger, which operates mainly as a shooting plunger, and pushes the plasticized material through the nozzle into the mold.

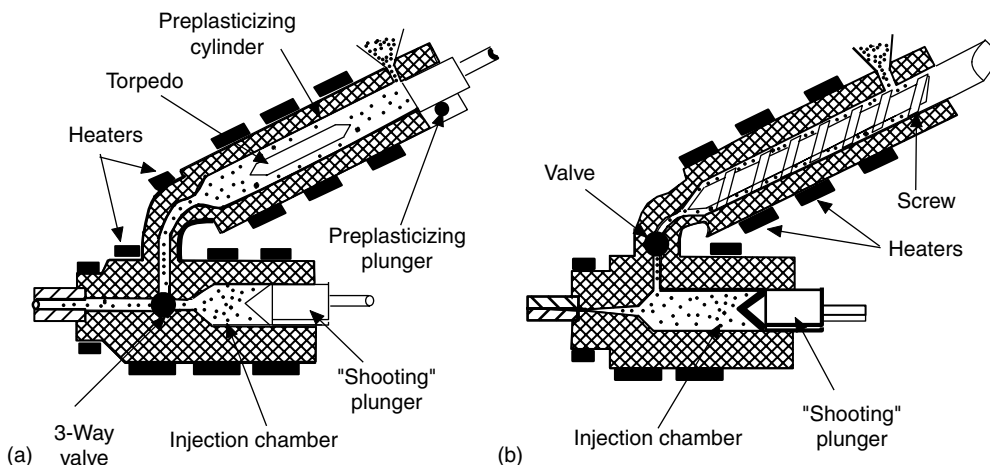


FIGURE 2.7 Schematic drawings of (a) a plunger-type preplasticizer and (b) a screw-type preplasticizer atop a plunger-type injection molding machine. (After Lukov, L. J. 1963. *SPE J.*, 13(10), 1057.)

Later, another variation of the two-stage plunger unit appeared, in which the first plunger stage was replaced by a rotation screw in a cylinder (Figure 2.7b). The screw increases the heat transfer at the walls and also does considerable heating by converting mechanical energy into heat. Another advantage of the screw is its mixing and homogenizing action. The screw feeds the melt into the second plunger unit, where the injection ram pushes it forward into the mold.

Although the single-stage plunger units (Figure 2.6) are inherently simple the limited heating rate has caused a decline in popularity: they have been mostly supplanted by the reciprocating screw-type machines. In these machines (Figure 2.8) the plunger and torpedo (or spreader) that are the key components of plunger-type machines are replaced by a rotating screw that moves back and forth like a plunger within the heating cylinder. As the screw rotates, the flights pick up the feed of granular material dropping from the hopper and force it along the heated wall of the barrel, thereby increasing the rate of heat transfer and also generating considerable heat by its mechanical work. The screw, moreover, promotes mixing and homogenization of the plastic material.

As the molten plastic comes off the end of the screw, the screw moves back to permit the melt to accumulate. At the proper time the screw is pushed forward without rotation, acting just like a plunger and forcing the melt through the nozzle into the mold. The size of the charge per shot is regulated by the back travel of the screw. The heating and homogenization of the plastics material are controlled by the screw rotation speed and wall temperatures.

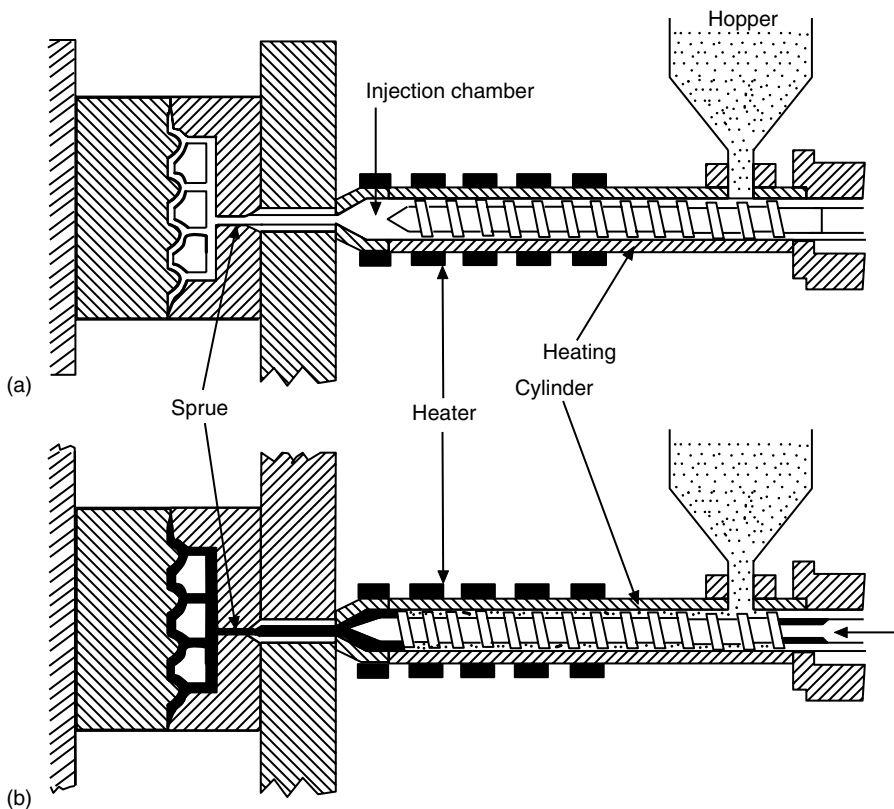


FIGURE 2.8 Cross-section of a typical screw-injection molding machine, showing the screw (a) in the retracted position and (b) in the forward position. (After Lukov, L. J. 1963. *SPE J.*, 13(10), 1057.)

2.5.2 Clamping Units

The clamping unit keeps the mold closed while plasticized material is injected into it and opens the mold when the molded article is ejected. The pressure produced by the injection plunger in the cylinder is transmitted through the column of plasticized material and then through the nozzle into the mold. The unlocking force, that is, the force which tends to open the mold, is given by the product of the injection pressure and the projected area of the molding. Obviously, the clamping force must be greater than the unlocking force to hold the mold halves closed during injection.

Several techniques can be used for the clamping unit: (1) hydraulic clamps, in which the hydraulic cylinder operates on the movable parts of the mold to open and close it; (2) toggle or mechanical clamps, in which the hydraulic cylinder operates through a toggle linkage to open and close the mold; and (3) various types of hydraulic mechanical clamps that combine features of (1) and (2).

Clamps are usually built as horizontal units, with injection taking place through the center of the stationary platen, although vertical clamp presses are also available for special jobs.

2.5.3 Molds

The mold is probably the most important element of a molding machine. Although the primary purpose of the mold is to determine the shape of the molded part, it performs several other jobs. It conducts the hot plasticized material from the heating cylinder to the cavity, vents the entrapped air or gas, cools the part until it is rigid, and ejects the part without leaving marks or causing damage. The mold design, construction, the craftsmanship largely determine the quality of the part and its manufacturing cost.

The injection mold is normally described by a variety of criteria, including (1) number of cavities in the mold; (2) material of construction, e.g., steel, stainless steel, hardened steel, beryllium copper, chrome-plated aluminum, and epoxy steel; (3) parting line, e.g., regular, irregular, two-plate mold, and three-plate mold; (4) method of manufacture, e.g., machining, hobbing, casting, pressure casting, electroplating, and spark erosion; (5) runner system, e.g., hot runner and insulated runner; (6) gating type, e.g., edge, restricted (pinpoint), submarine, sprue, ring, diaphragm, tab, flash, fan, and multiple; and (7) method of ejection, e.g., knockout (KO) pins, stripper ring, stripper plate, unscrewing cam, removable insert, hydraulic core pull, and pneumatic core pull.

2.5.3.1 Mold Designs

Molds used for injection molding of thermoplastic resins are usually flash molds, because in injection molding, as in transfer molding, no extra loading space is needed. However, there are many variations of this basic type of mold design.

The design most commonly used for all types of materials is the two plate design (Figure 2.9). The cavities are set in one plate, the plungers in the second plate. The sprue bushing is incorporated in that plate mounted to the stationary half of the mold. With this arrangement it is possible to use a direct center gate that leads either into a single-cavity mold or into a runner system for a multi-cavity mold. The plungers are ejector assembly and, in most cases, the runner system belongs to the moving half of the mold. This is the basic design of an injection mold, though many variations have been developed to meet specific requirements.

A three-plate mold design (Figure 2.10) features a third, movable, plate which contains the cavities, thereby permitting center or offset gating into each cavity for multicavity operation. When the mold is opened, it provides two openings, one for ejection of the molded part and the other for removal of the runner and sprue.

Moldings with inserts or threads or coring that cannot be formed by the normal functioning of the press require installation of separate or loose details or cores in the mold. These loose members are ejected with the molding. They must be separated from the molding and reinstalled in the mold after every cycle. Duplicate sets are therefore used for efficient operation.

Hydraulic or pneumatic cylinders may be mounted on the mold to actuate horizontal coring members. It is possible to mold angular coring, without the need for costly loose details, by adding angular core pins

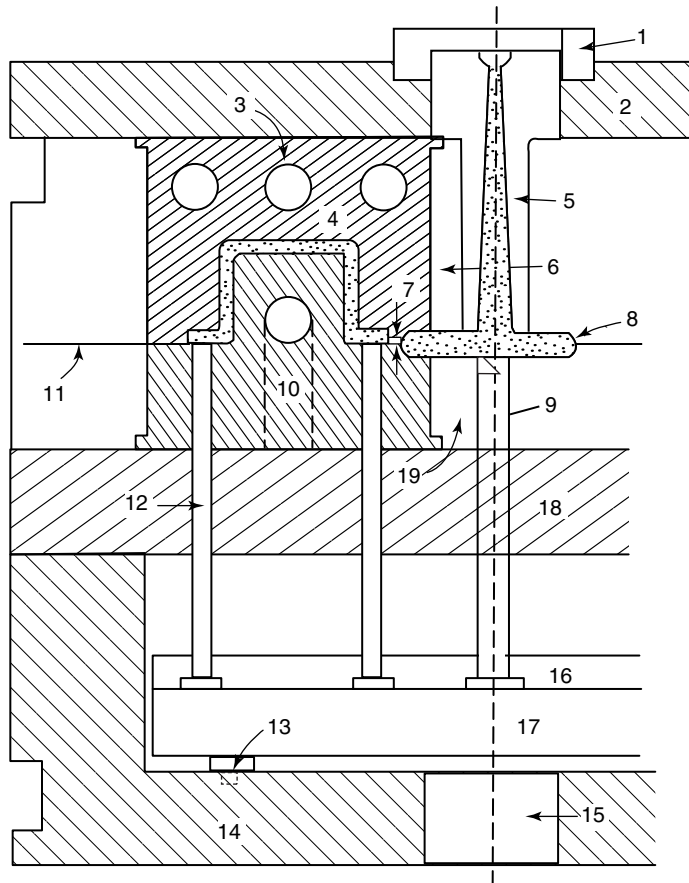


FIGURE 2.9 A two-plate injection-mold design: (1) locating ring; (2) clamping plate; (3) water channels; (4) cavity; (5) sprue bushing; (6) cavity retainer; (7) gate; (8) full round runner; (9) sprue puller pin; (10) plunger; (11) parting runner; (12) ejector pin; (13) stop pin; (14) ejector housing; (15) press ejector clearance; (16) pin plate; (17) ejector bar; (18) support plate; (19) plunger retainer.

engaged in sliding mold members. Several methods may be used for unscrewing internal or external threads on molded parts: For high production rates automatic unscrewing may be done at relatively low cost by the use of rack-and-gear mechanism actuated by a double-acting hydraulic long-stroke cylinder. Other methods of unscrewing involve the use of an electric gear-motor drive or friction-mold wipers actuated by double-acting cylinders. Parts with interior undercuts can be made in a mold which has provision for angular movement of the core, the movement being actuated by the ejector bar that frees the metal core from the molding.

2.5.3.2 Number of Mold Cavities

Use of multiple mold cavities permits greater increase in output speeds. However, the greater complexity of the mold also increases significantly the manufacturing cost. Note that in a single-cavity mold the limiting factor is the cooling time of the molding, but with more cavities in the mold the plasticizing capacity of the machine tends to be the limiting factor. Cycle times therefore do not increase prorata with the number of cavities.

There can be no clear-cut answer to the question of optimum number of mold cavities, since it depends on factors such as the complexity of the molding, the size and type of the machine, cycle time,

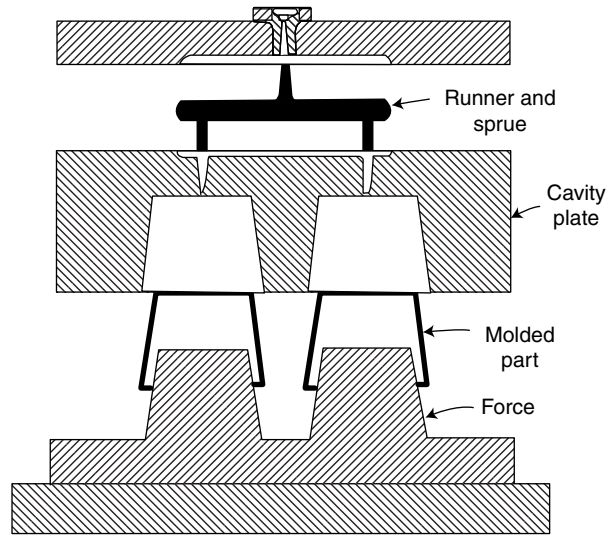


FIGURE 2.10 A diagram of a three-plate injection mold.

and the number of moldings required. If a fairly accurate estimate can be made of the costs and cycle time for molds with each possible number of cavities and a cost of running the machine (with material) is assumed, a break-even quantity of the number of moldings per hour can be calculated and compared with the total production required.

2.5.3.3 Runners

The channels through which the plasticized material enters the gate areas of the mold cavities are called *runners*. Normally, runners are either full round or trapezoidal in cross section. Round cross section offers the least resistance to the flow of material but requires a duplicate machining operation in the mold, since both plates must be cut at the parting line. In three-plate mold designs, however, trapezoidal runners are preferred, since sliding movements are required across the parting-line runner face.

One can see from Figure 2.10 that a three-plate mold operation necessitates removal of the runner and sprue system, which must be reground, and the material reused. It is possible, however, to eliminate the runner system completely by keeping the material in a fluid state. This mold is called a *hot-runner mold*. The material is kept fluid by the hot-runner manifold, which is heated with electric cartridges.

The advantage of a hot-runner mold is that in a long-running job it is the most economical way of molding—there is not regrinding, with its attendant cost of handling and loss of material, and the mold runs automatically, eliminating variations caused by operators. A hot-runner mold also presents certain difficulties: It takes considerably longer to become operational, and in multicavity molds balancing the gate and the flow and preventing drooling are difficult. These difficulties are partially overcome in an insulated-runner mold, which is a cross between a hot-runner mold and a three-plate mold and has no runner system to regrind. An insulated-runner mold is more difficult to start and operate than a three-plate mold, but it is considerably easier than a hot-runner mold.

2.5.3.4 Gating

The gate provides the connection between the runner and the mold cavity. It must permit enough material to flow into the mold to fill out the cavity. The type of the gate and its size and location in the mold strongly affect the molding process and the quality of the molded part. There are two types of gates: large and restricted. Restricted (pinpointed) gates are usually circular in cross section and for most

thermoplastics do not exceed 0.060 in. in diameter. The apparent viscosity of a thermoplastic is a function of shear rate—the viscosity decreases as the shear rate and, hence, the velocity increases. The use of the restricted gate is therefore advantageous, because the velocity of the plastic melt increases as it is forced through the small opening; in addition, some of the kinetic energy is transformed into heat, raising the local temperature of the plastic and thus further reducing its viscosity. The passage through a restricted area also results in higher mixing.

The most common type of gate is the edge gate (Figure 2.11a), where the part is gated either as a restricted or larger gate at some point on the edge. The edge gate is easy to construct and often is the only practical way of gating. It can be fanned out for large parts or when there is a special reason. Then it is called a fan gate (Figure 2.11b). When it is required to orient the flow pattern in one direction, a flash gate (Figure 2.11c) may be used. It involves extending the fan gate over the full length of the part but keeping it very thin.

The most common gate for single-cavity molds is the sprue gate (Figure 2.11d). It feeds directly from the nozzle of the machine into the molded part. The pressure loss is therefore a minimum. But the sprue gate has the disadvantages of the lack of a cold slug, the high stress concentration around the gate area, and the need for gate removal. A diaphragm gate (Figure 2.11e) has, in addition to the sprue, a circular area leading from the sprue to the piece. This type of gate is suitable for gating hollow tubes. The diaphragm eliminates stress concentration around the gate because the whole area is removed, but the cleaning of this gate is more difficult than for a sprue gate. Ring gates (Figure 2.11f) accomplish the same purpose as gating internally in a hollow tube, but from the outside.

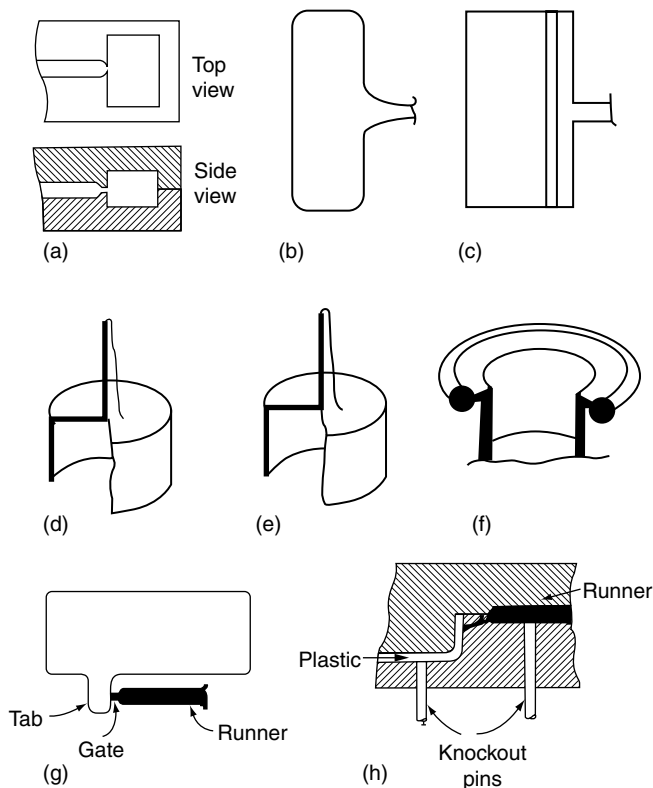


FIGURE 2.11 Gating design: (a) edge; (b) fan; (c) flash; (d) sprue; (e) diaphragm; (f) ring; (g) tab; (h) submarine.

When the gate leads directly into the part, there may be surface imperfection due to jetting. This may be overcome by extending a tab from the part into which the gate is cut. This procedure is called tab gating (Figure 2.14g). The tab has to be removed as a secondary operation.

A submarine gate (Figure 2.11h) is one that goes through the steel of the cavity. It is very often used in automatic molds.

2.5.3.5 Venting

When the melted plastic fills the mold, it displaces the air. The displaced air must be removed quickly, or it may ignite the plastic and cause a characteristic burn, or it may restrict the flow of the melt into the mold cavity, resulting in incomplete filling. For venting the air from the cavity, slots can be milled, usually opposite the gate. The slots usually range from 0.001 to 0.002 in. deep and from 3/8 to 1 in. wide. Additional venting is provided by the clearance between KO pins and their holes. Note that the gate location is directly related to the consideration of proper venting.

2.5.3.6 Parting Line

If one were inside a closed mold and looking outside, the mating junction of the mold cavities would appear as a line. It also appears as a line on the molded piece and is called the parting line. A piece may have several parting lines. The selection of the parting line in mold design is influenced by the type of mold, number of cavities, shape of the piece, tapers, method of ejection, method of fabrication, venting, wall thickness, location and type of gating, inserts, postmolding operations, and aesthetic consideration.

2.5.3.7 Cooling

The mold for thermoplastics receives the molten plastic in its cavity and cools it to solidity to the point of ejection. The most is provided with cooling channels. The mold temperature is controlled by regulating the temperature of the cooling fluid and its rate of flow through the channels. Proper cooling or coolant circulation is essential for uniform repetitive mold cycling.

The functioning of the mold and the quality of the molded part depend largely on the location of the cooling channel. Since the rate of heat transfer is reduced drastically by the interface of two metal pieces, no matter how well they fit, cooling channels should be located in cavities and cores themselves rather than only in the supporting plates. The cooling channels should be spaced evenly to prevent uneven temperatures on the mold surface. They should be as close to the plastic surface as possible, taking into account the strength of the mold material. The channels are connected to permit a uniform flow of the cooling or heating medium, and they are thermostatically controlled to maintain a given temperature.

Another important factor in mold temperature control is the material the mold is made from. Beryllium copper has a high thermal conductivity, about twice that of steel and four times that of stainless steel. A beryllium copper cavity should thus cool about four times as fast as a stainless steel one. A mold made of beryllium copper would therefore run significantly faster than one of stainless steel.

2.5.3.8 Ejection

Once the molded part has cooled sufficiently in the cavity, it has to be ejected. This is done mechanically by KO pins, KO sleeves, stripper plates, stripper rings or compressed air, used either singly or in combination. The most frequent problem in new molds is with ejection. Because there is no mathematical way of predicting the amount of ejection force needed, it is entirely a matter of experience.

Since ejection involves overcoming the forces of adhesion between the mold and the plastic, the area provided for the knockout (KO) is an important factor. If the area is too small, the KO force will be concentrated, resulting in severe stresses on the part. As a result, the part may fail immediately or in later service. In materials such as ABS and high-impact polystyrene, the severe stresses can also discolor the plastic.

Sticking in a mold makes ejection difficult. Sticking is often related to the elasticity of steel and is called packing. When injection pressure is applied to the molten plastic and force it into the mold, the steel

deforms; when the pressure is relieved, the steel retracts, acting as a clamp on the plastic. Packing is often eliminated by reducing the injection pressure and/or the injection forward time. Packing is a common problem in multicavity molds and is caused by unequal filling. Thus, if a cavity seals off without filling, the material intended for the cavity is forced into other cavities, causing overfilling.

2.5.3.9 Standard Mold Bases

Standardization of mold bases for injection molding, which was unknown prior to 1940, was an important factor in the development of efficient mold making. Standard mold bases were pioneered by the D-M-E Co., Michigan, to provide the mold maker with a mold base at lower cost and with much higher quality than if the base were manufactured by the mold maker. Replacement parts, such as locating ring and sprue bushings, loader pins and bushings, KO pins and push-back pins of high quality are also available to the molder. Since these parts are common for many molds, they can be stocked by the molder in the plant and thus down time is minimized. An exploded view of the components of a standard injection-mold base assembly is shown in Figure 2.12.

2.5.4 Structural Foam Injection Molding

Structural foam injection molding produces parts consisting of solid external skin surfaces surrounding an inner cellular (or foam) core, as shown in Figure 2.13. Large, thick structural foam parts can be produced by this process with both low and high pressure and using either nitrogen gas or chemical blowing agents (see “[Foaming Process](#)”).

2.5.5 Co-Injection (Sandwich) Molding

Co-injection molding is used to produce parts that have a laminated structure with the core material embedded between the layers of the skin material. As shown in Figure 2.14, the process involves sequential injection of two different but compatible polymer melts into a cavity where the materials

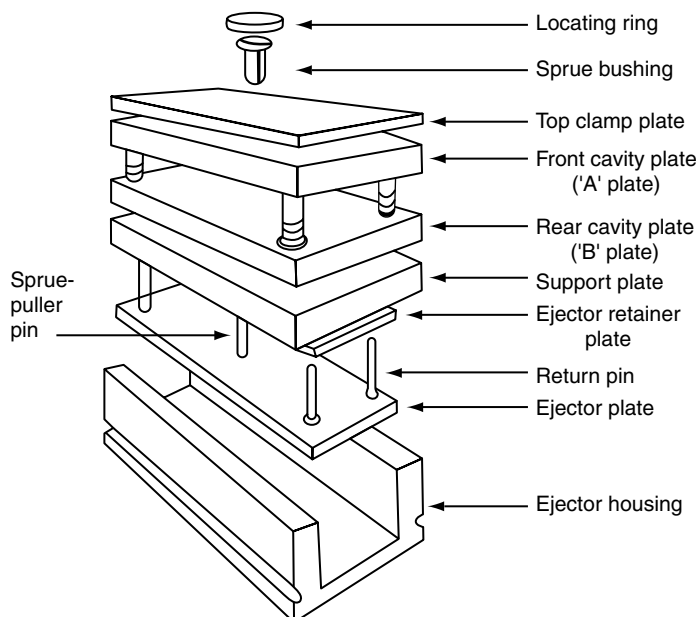


FIGURE 2.12 Exploded view of a standard mold base showing component parts.

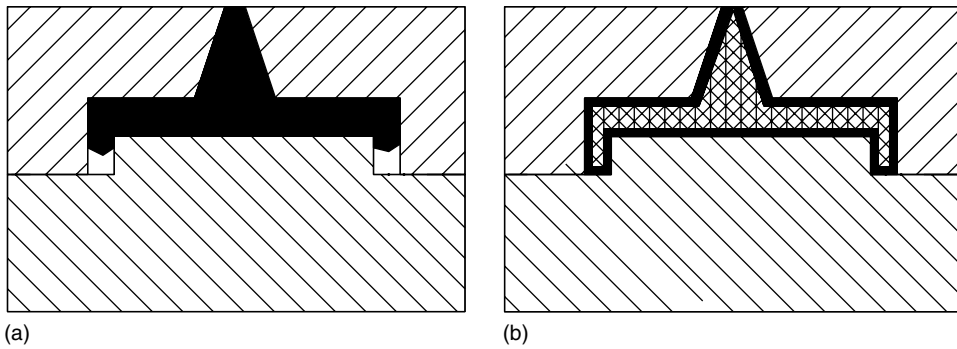


FIGURE 2.13 Structural foam injection molding. (a) During injection under high pressure there is very little foaming. (b) After injection, pressure drops and foaming occurs at hot core.

laminate and solidify. A short shot of skin polymer melt is first injected into the mold (Figure 2.14a), followed by core polymer melt which is injected until the mold cavity is nearly filled (Figure 2.14b); the skin polymer is then injected again to purge the core polymer away from the sprue (Figure 2.14c). The process offers the inherent flexibility of using the optimal properties of each material or modifying the properties of each material or those of the molded part.

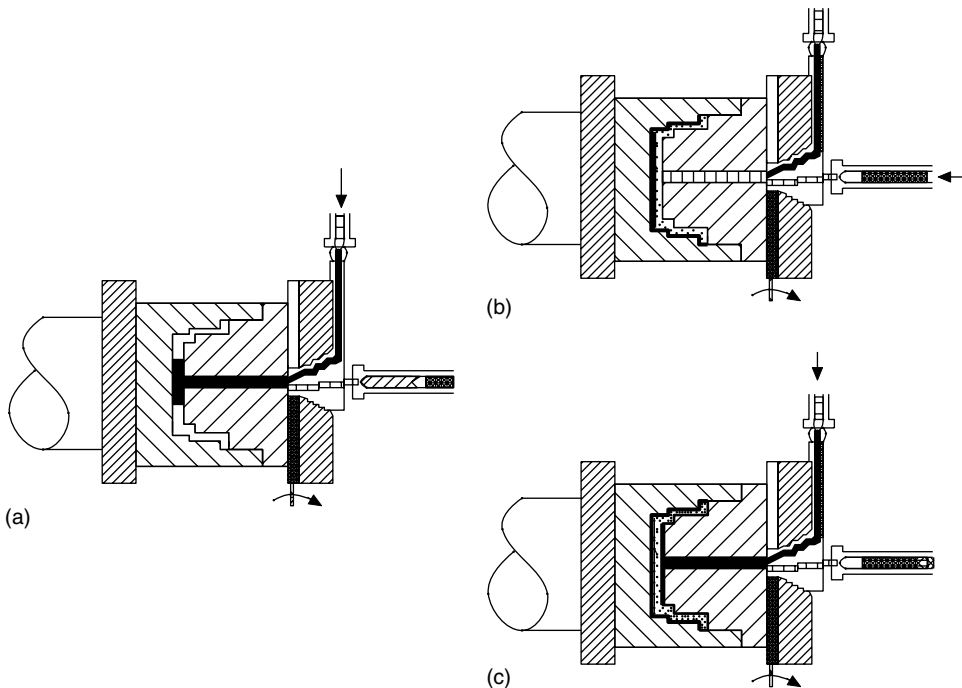


FIGURE 2.14 Three stages of co-injection (sandwich) molding. (a) Short shot of skin polymer melt (shown in black) is injected into the mold; (b) injection of core polymer melt until cavity is nearly filled; and (c) skin polymer melt is injected again, pushing the core polymer away from the sprue.

2.5.6 Gas-Assisted Injection Molding

The gas-assisted injection molding process begins with a partial or full injection of polymer melt into the mold cavity. Compressed gas is then injected into the core of the polymer melt to help fill and pack the mold, as shown in Figure 2.15 for the Asahi Gas Injection Molding process. This process is thus capable of producing hollow rigid parts, free of sink marks. The hollowing out of thick sections of moldings results in reduction in part weight and saving of resin material.

Other advantages include shorter cooling cycles, reduced clamp force tonnage and part consolidation. The process allows high precision molding with greater dimensional stability by eliminating uneven mold shrinkage and makes it possible to mold complicated shapes in single form, thus reducing product assembly work and simplifying mold design.

The formation of thick walled sections of a molding can be easily achieved by introducing gas in the desired locations. The gas channels thus formed also effectively support the flow of resin, allowing the molding pressure to be greatly reduced, which in turn reduces internal stresses, allows uniform mold shrinkage, and reduces sink marks and warpage.

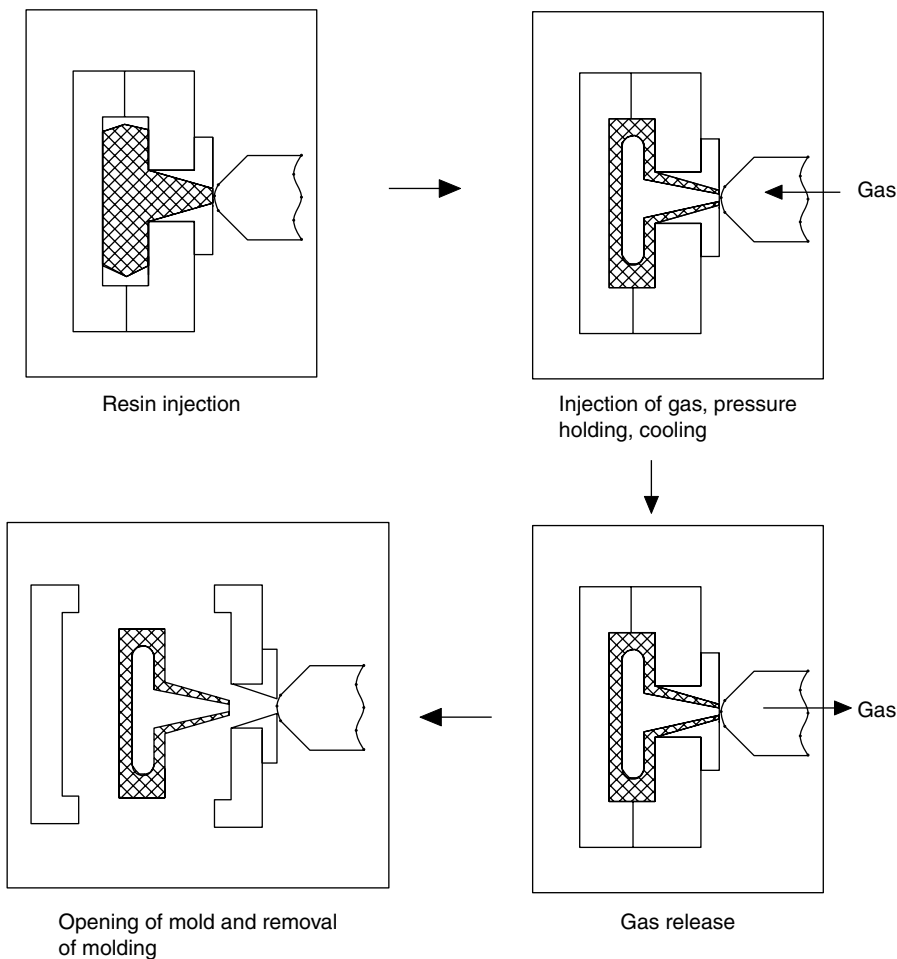


FIGURE 2.15 Schematic of the Asahi Gas Injection (AGI) molding process.

2.6 Injection Molding of Thermosetting Resins

2.6.1 Screw-Injection Molding of Thermosetting Resins

The machines used earlier were basically plunger-type machines [6,10–12]. But in the late 1960s' shortly after the development of screw-transfer machines, the concept of screw-injection molding of thermosets, also known as direct screw transfer (or DST), was introduced. The potential of this techniques for low-cost, high-volume production of molded thermoset parts was quickly recognized, and today screw-injection machines are available in all clamp tonnages up to 1,200 tons and shot sizes up to 10 lb. Coupled with this, there has been a new series of thermosetting molding materials developed specifically for injection molding. These materials have long life at moderate temperature (approximately 200°F), which permits plastication in screw barrel, and react (cure) very rapidly when the temperature is raised to 350°F–400°F (177°–204°C), resulting in reduced cycle time.

A typical arrangement for a direct screw-transfer injection-molding machine for thermosets is shown in Figure 2.16. The machine has two sections mounted on a common base. One section constitutes the plasticizing and injection unit, which includes the feed hopper, the heated barrel that encloses the screw, the hydraulic cylinder which pushes the screw forward to inject the plasticized material into the mold, and a motor to rotate the screw. The other section clamps and holds the mold halves together under pressure during the injection of the hot plastic melt into the mold.

The thermosetting material (in granular or pellet form) suitable for injection molding is fed from the hopper into the barrel and is then moved forward by the rotation of the screw. During its passage, the material receives conductive heat from the wall of the heated barrel and frictional heat from the rotation of the screw. For thermosetting materials, the screw used is a zero-compression-ratio screw—i.e., the depths of flights of the screw at the feed-zone end and at the nozzle end are the same. By comparison, the screws used in thermoplastic molding machines have compression ratios such that the depth of flight at the feed end is one and one-half to five times that at the nozzle end. This difference in screw configuration is a major difference between thermoplastic- and thermosetting-molding machines.

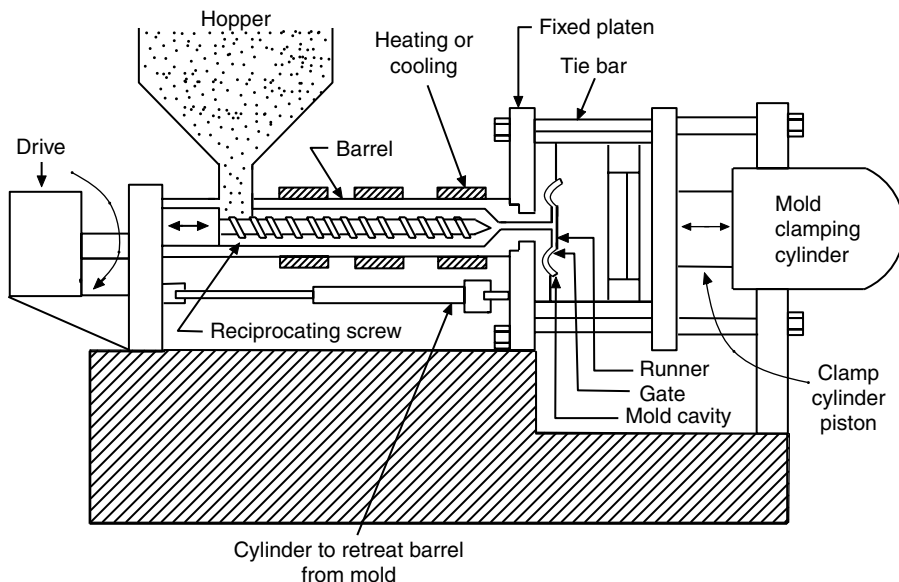


FIGURE 2.16 Schematic of a direct screw-transfer molding machine for thermosets. (After Frados, J. ed. 1976. *Plastics Engineering Handbook*, 4th Ed., Van Nostrand Reinhold, New York.)

As the material moves forward in the barrel due to rotation of the screw, it changes in consistency from a solid to semifluid, and as it starts accumulating at the nozzle end, it exerts a backward pressure on the screw. This back pressure is thus used as a processing variable. The screw stops turning when the required amount of material—the charge—has accumulated at the nozzle end of the barrel, as sensed by a limit switch. (The charge is the exact volume of material required to fill the sprue, runners, and cavities of the mold.) the screw is then moved forward like a plunger by hydraulic pressure (up to 20,000 psi) to force the hot plastic melt through the sprue of the mold and into the runner system, gates, and mold cavities. The nozzle temperature is controlled to maintain a proper balance between a hot mold (350°F–400°F), and a relatively cool barrel (150°F–200°F).

Molded-in inserts are commonly used with thermosetting materials. However, since the screw-injection process is automatic, it is desirable to use postassembled inserts rather than molded-in inserts because molded-in inserts require that the mold be held open each cycle to place the inserts. A delay in the manual placement disrupts an automatic cyclic operation, affecting both the production rate and the product quality.

Tolerances of parts made by injection molding of thermosetting materials are comparable to those produced by the compression and transfer methods described, earlier. Tolerances achieved are as low as ± 0.001 in./in., although ordinarily tolerance of ± 0.003 – 0.005 in./in. are economically practical.

Thermosetting materials used in screw-injection molding are modified from conventional thermosetting compounds. These modifications are necessary to provide the working time-temperature relationship required for screw plasticating. The most commonly used injection-molding thermosetting materials are the phenolics. Other thermosetting materials often molded by the screw-injection process include melamine, urea, polyester, alkyd, and diallyl phthalate (DAP).

Since the mid-1970s the injection molding of glass-fiber-reinforced thermosetting polyesters gained increasing importance as better materials (e.g., low shrinkage resins, palletized forms of polyester/glass, etc.), requirement, and tooling became available. Injection-molded reinforced thermoset plastics have thus made inroads in such markets as switch housings, fuse blocks, distributor caps, power-tool housings, office machines, etc. Bulk molding compounds (BMC), which are puttylike FRP (fibrous glass-reinforced plastic) materials, are injection molded to make substitutes of various metal die castings.

For injection molding, FRP should have some specific characteristics. For example, it must flow easily at lower-than-mold temperatures without curing and without separating into resin, glass, and filler components, and it should cure rapidly when in place at mold temperature. A traditional FRP material shrinks about 0.003 in./in. during molding, but low-shrink FRP materials used for injection molding shrink as little as 0.000–0.0005 in./in. Combined with proper tooling, these materials thus permit production of pieces with dimensional tolerances of ± 0.0005 in./in.

Proper design of parts for injection molding requires an understanding of the flow characteristics of material within the mold. In this respect, injection-molded parts of thermosets are more like transfer-molded parts than to compression-molded parts. Wall-section uniformity is an important consideration in part design. Cross sections should be as uniform as possible, within the dictates of part requirements, since molding cycles, and therefore costs, depend on the cure time of the thickest section. (For thermoplastics, however, it is the cooling time that is critical). A rule of thumb for estimating cycle times for a 1/4-in. wall section is 30 sec for injection-molded thermosets (compared to 45 sec for thermoplastics). As a guideline for part design, a good working average for wall thickness is 1/8–3/16 in., with a minimum of 1/16 in.

2.7 Extrusion

The extrusion process is basically designed to continuously convert a soft material into a particular form [13–15]. An oversimplified analogy may be a house-hold meat grinder. However, unlike the extrudate from a meat grinder, plastic extrudates generally approach truly continuous formation. Like the usual meat grinder, the extruder (Figure 2.17) is essentially a screw conveyor. It carries the cold plastic material

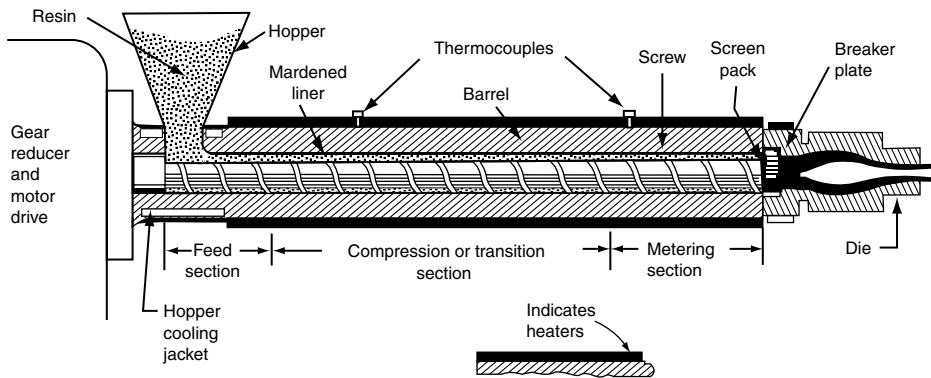


FIGURE 2.17 Scheme for a typical single-screw extruder showing extruding pipe.

(in granular or powdered form) forward by the action of the screw, squeezes it, and, with heat from external heaters and the friction of viscous flow, changes it to a molten stream. As it does this, it develops pressure on the material, which is highest right before the molten plastic enters the die. The screen pack, consisting of a number of fine or coarse mesh gauzes supported on a breaker plate and placed between the screw and the die, filter out dirt and unfused polymer lumps. The pressure on the molten plastic forces it through an adapter and into the die, which dictates the shape of the fine extrudate. A die with a round opening as shown in Figure 2.17, produces pipe; a square die opening produces a square profile, etc. Other continuous shapes, such as the film, sheet, rods, tubing, and filaments, can be produced with appropriate dies. Extruders are also used to apply insulation and jacketing to wire and cable and to coat substrates such as paper, cloth, and foil.

When thermoplastic polymers are extruded, it is necessary to cool the extrudate below T_m or T_g to impart dimensional stability. This cooling can often be done simply by running the product through a tank of water, by spraying cold water, or, even more simply, by air cooling. When rubber is extruded, dimensional stability results from cross-linking (vulcanization). Interestingly, rubber extrusion for wire coating was the first application of the screw extruder in polymer processing.

Extruders have several other applications in polymer processing: in the blowmolding process they are used to make hollow objects such as bottles; in the blow-film process they are used for making wide films; they are also used for compounding plastics (i.e., adding various ingredients to a resin mix) and for converting plastics into the pellet shape commonly used in processing. In this last operation specialized equipment, such as the die plate-cutter assembly, is installed in place of the die, and an extrusion-type screw is used to provide plasticated melt for various injection-molding processes.

2.7.1 Extruder Capacity

Standard sizes of single-screw extruders are $1\frac{1}{2}$, 2, $2\frac{1}{2}$, $3\frac{1}{4}$, $3\frac{1}{2}$, $4\frac{1}{2}$, 6, and 8 in., which denote the inside diameter (ID) of the barrel. As a rough guide, extruder capacity Q_e , in pounds per hour, can be calculated from the barrel diameter D_b , in inches, by the empirical relation [15]

$$Q_e = 16D_b^{2.2} \quad (2.1)$$

Another estimate of extruder capacity can be made by realizing that most of the energy needed to melt the thermoplastic stems from the mechanical work, whereas the barrel heaters serve mainly to insulate the material. If we allow an efficiency from drive to screw of about 80%, the capacity Q_e (lb/h) can be approximately related to the power supplied H_p (horsepower), the heat capacity of the material C_p [Btu/lb °F], and the temperature rise from feed to extrudate ΔT (°F) by

$$Q_e = 1.9 \times 10^3 H_p / C_p \Delta T \quad (2.2)$$

Equation 2.2 is obviously not exact since the heat of melting and other thermal effects have been ignored. Equation 2.2 coupled with Equation 2.1 enables one to obtain an estimate of ΔT . Thus, for processing of poly(methyl methacrylate), for which C_p is about 0.6 Btu/lb °F, in a 2-in. extruder run by a 10-hp motor, Equation 2.1 gives $Q_e = 74$ lb/h, and Equation 2.2 indicates that $\Delta T \cong 430^\circ\text{F}$. In practice, a ΔT of 350°F is usually adequate for this polymer.

2.7.2 Extruder Design and Operation

The most important component of any extruder is the screw. It is often impossible to extruder satisfactorily one material by using a screw designed for another material. Therefore screw designs vary with each material.

2.7.2.1 Typical Screw Construction

The screw consists of a steel cylinder with a helical channel cut into it (Figure 2.18). The helical ridge formed by the machining of the channel is called the flight, and the distance between the flights is called the lead. The lead is usually constant for the length of the screw in single-screw machines. The helix angle is called pitch. Helix angles of the screw are usually chosen to optimize the feeding characteristics. An angle of 17.5° is typical, though it can be varied between 12° and 20° . The screw outside diameter is generally just a few thousandths of an inch less than the ID of the barrel. The minimal clearance between screw and barrel ID prevents excessive buildup of resin on the inside barrel wall and thus maximizes heat transfer.

The screw may be solid or cored. Coring is used for steam heating or, more often, for water cooling. Coring can be for the entire length of the screw or for a portion of it, depending on the particular application. Full length coring of the screw is used where large amounts of heat are to be removed. The screw is cored only in the initial portions at the hopper end when the objective is to keep the feed zone cooler for resins which tend to soften easily. Screws are often fabricated from 4140 alloy steel, but other materials are also used. The screw flights are usually hardened by flame-hardening techniques or inset with a wear resistant alloy (e.g., Stellite 6).

2.7.2.2 Screw Zones

Screws are characterized by their length-diameter ratio (commonly written as L/D ratios). L/D ratios most commonly used for single-screw extruders range from 15:1 to 30:1. Ratios of 20:1 and 24:1 are common for thermoplastics, whereas lower values are used for rubbers. A long barrel gives a more homogeneous extrudate, which is particularly desirable when pigmented materials are handled. Screws are also characterized by their compression ratios—the ratio of the flight depth of the screw at the hopper end to the flight depth at the die end. Compression ratios of single-screw extruders are usually 2:1–5:1.

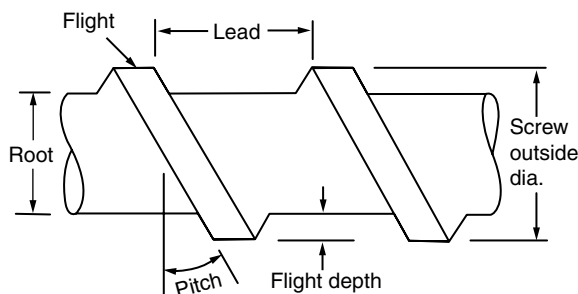


FIGURE 2.18 Detail of screw.

The screw is usually divided into three sections, namely, feed, compression, and metering (Figure 2.17). One of the basic parameters in screw design involves the ratio of lengths between the feed, compression (or transition), and metering sections of the screw. Each section has its own special rate. The feed section picks up the powder, pellets, or beads from under the hopper mouth and conveys them forward in the solid state to the compression section. The feed section is deep flighted so that it functions in supplying enough material to prevent starving the forward sections.

The gradually diminishing flight depth in the compression section causes volume compression of the melting granules. The volume compression results in the trapped air being forced back through the feed section instead of being carried forward with the resin, thus ensuring an extrudate free from porosity. Another consequence of volume compression is an increase in the shearing action on the melt, which is caused by the relative motion of the screw surfaces with respect to the barrel wall. The increased shearing action produces good mixing and generates frictional heat, which increases fluidity of the melt and leads to a more uniform temperature distribution in the molten extrudate. The resin should be fully melted into a reasonably uniform melt by the time it enters the final section of the screw, known as the metering section. The function of the metering section is to force the molten polymer through the die at a steady rate and iron out pulsations. For many screw designs the compression ratio is 3–5; i.e., the flight depth in the metering section is one-third to one-fifth that in the feed section.

2.7.2.3 Motor Drive

The motor employed for driving the screw of an extruder should be of more than adequate power required for its normal needs. Variable screw speeds are considered essential. Either variable-speed motors or constant-speed motors with variable-speed equipment, such as hydraulic systems, step-change gear boxes, and infinitely variable-speed gear boxes may be used. Thrust bearings of robust construction are essential because of the very high back pressure generated in an extruder and the trend towards higher screw speeds. Overload protection in the form of an automatic cut-out should be fitted.

2.7.2.4 Heating

Heat to melt the polymer granules is supplied by external heaters or by frictional heat generated by the compression and shearing action of the screw on the polymer. Frictional heat is considerable, and in modern high-speed screw extruders it supplies most of the heat required for steady running. External heaters serve only to insulate the material and to prevent the machine from stalling at the start of the run when the material is cold. The external heater may be an oil, steam, or electrical type. Electrical heating is most popular because it is compact, clean, and accurately controlled. Induction heating is also used because it gives quicker heating with less variation and facilitates efficient cooling.

The barrel is usually divided into three or four heating zones; the temperature is lowest at the feed end and highest at the die end. The temperature of each zone is controlled by carefully balancing heating and cooling. Cooling is done automatically by either air or water. (The screw is also cored for heating and cooling.) The screw is cooled where the maximum amount of compounding is required, because this improves the quality of the extrudate.

2.7.2.5 Screw Design

The screw we have described is a simple continuous-flight screw with constant pitch. The more sophisticated screw designs include flow disrupters or mixing sections (Figure 2.19). These mixer screws have mixing sections which are designed as mechanical means to break up and rearrange the laminar flow of the melt within the flight channel, which results in more thorough melt mixing and more uniform heat distribution in the metering section of the screw.

Mixer screws have also been used to mix dissimilar materials (e.g., resin and additives or simply dissimilar resins) and to improve extrudate uniformity at higher screw speeds (> 100 rpm). A few typical mixing section designs are shown in Figure 2.20. The fluted-mixing-section-barrier-type design (Figure 2.20a) has proved to be especially applicable for extrusion of polyolefins. For some mixing problems, such as pigment mixing during extrusion, it is convenient to use rings (Figure 2.20b)

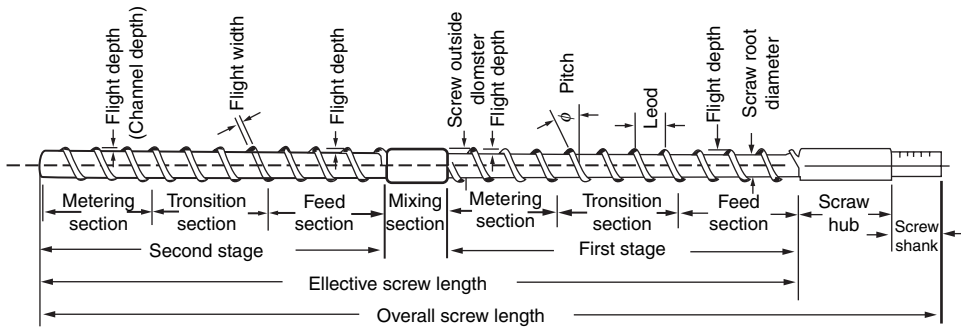


FIGURE 2.19 Single-flight, two-stage extrusion screw with mixing section.

or mixing pins (Figure 2.20c) and sometimes parallel interrupted mixing flights having wide pitch angles (Figure 2.20d).

A later development in extruder design has been the use of venting or degassing zones to remove any volatile constituents from the melt before it is extruded through the die. This can be achieved by placing an obstruction in the barrel (the reverse flights in Figure 2.21) and by using a valved bypass section to step down the pressure developed in the first stage to atmospheric pressure for venting. In effect, two screws are used in series and separated by the degassing or venting zone. Degassing may also be achieved by having a deeper thread in the screw in the degassing section than in the final section of the first screw, so the polymer melt suddenly finds itself in an increased volume and hence is at a lower pressure. The volatile vapors released from the melt are vented through a hold in the top of the extruder barrel or through a hollow core of the screw by way of a hole drilled in the trailing edge of one of the flights in the degassing zone. A vacuum is sometimes applied to assist in the extraction of the vapor. Design and operation must be suitably controlled to minimize plugging of the vent (which, as noted above, is basically an open area) or the possibility of the melt escaping from this area.

Many variations are possible in screw design to accommodate a wide range of polymers and applications. So many parameters are involved, including such variables as screw geometry, materials characteristics, operating conditions, etc., that the industry now uses computerized screw design, which permits analysis of the variables by using mathematical models to derive optimum design of a screw for a given application.

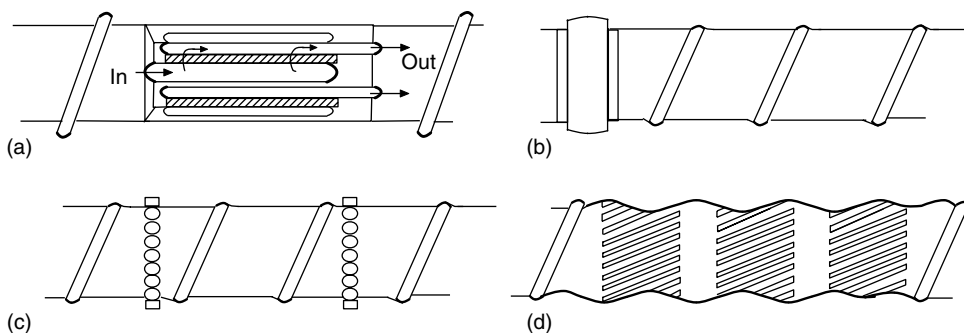


FIGURE 2.20 Mixing section designs: (a) fluted-mixing-section-barrier type; (b) ring-barrier type; (c) mixing pins; (d) parallel interrupted mixing flights. (After Frados, J. ed. 1976. *Plastics Engineering Handbook*, 4th Ed., Van Nostrand Reinhold, New York.)

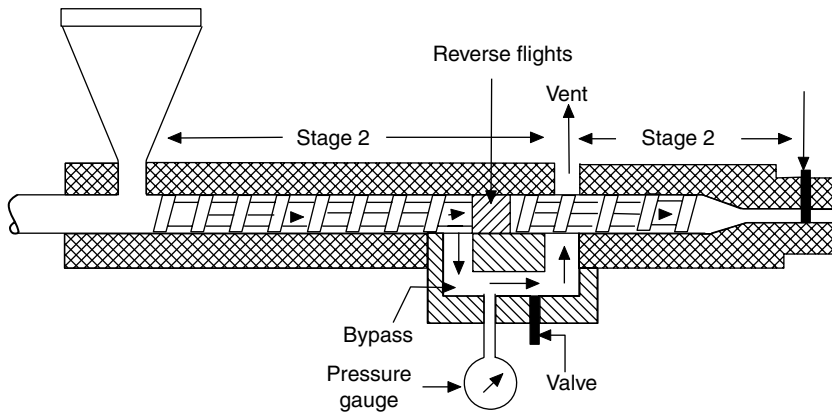


FIGURE 2.21 A two-stage vented extruder with a valved bypass. (After Fisher, E. G. 1971. *Blow Molding of Plastics*. Iliffe, London.)

Various screw designs have been recommended by the industry for extrusion of different plastics. For polyethylene, for example, the screw should be long with an L/D of at least 16:1 or 30:1 to provide a large area for heat transfer and plastication. A constant-pitch, decreasing-channel-depth, metering-type polyethylene screw or constant-pitch, constant-channel-depth, metering-type nylon screw with a compression ratio between 3–1 and 4–1 (Figure 2.22) is recommended for polyethylene extrusion, the former being preferable for film extension and extrusion coating. Nylon-6, 6 melts at approximately 260°C (500°F). Therefore, an extruder with an L/D of at least 16:1 is necessary. A screw with a compression ratio of 4:1 is recommended.

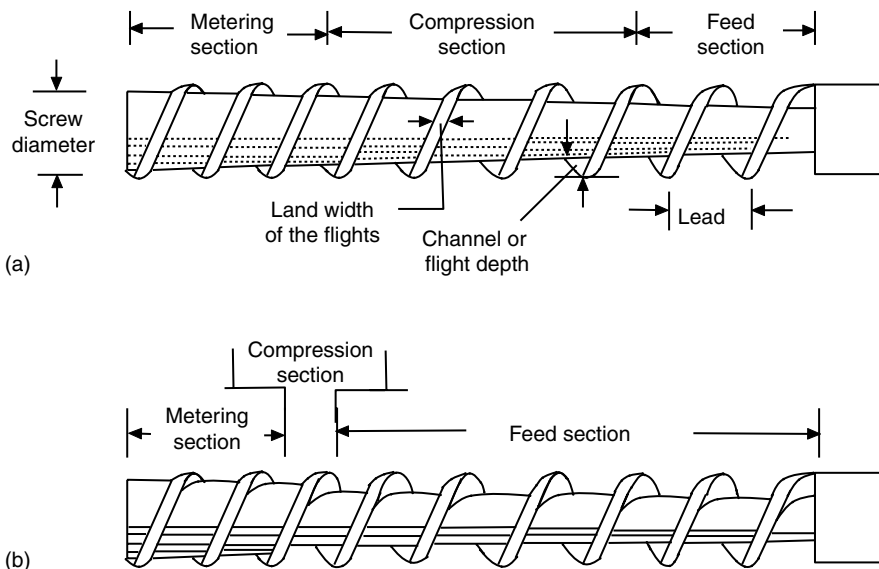


FIGURE 2.22 (a) Constant pitch, decreasing channel depth, metering-type polyethylene screw. (b) Constant pitch, constant-channel-depth, metering-type nylon screw (not to scale). (After Frados, J. ed. 1976. *Plastics Engineering Handbook*, 4th Ed., Van Nostrand Reinhold, New York.)

2.7.3 Multiple-Screw Extruders

Multiple-screw extruders (that is, extruders with more than a single screw) were developed largely as a compounding device for uniformly blending plasticizers, fillers, pigments, stabilizers, etc., into the polymer. Subsequently, the multiple-screw extruders also found use in the processing of plastics.

Multiple-screw extruders differ significantly from single-screw extruders in mode of operation. In a single-screw machine, friction between the resin and the rotating screw, makes the resin rotate with the screw, and the friction between the rotating resin and the barrel pushes the material forward, and this also generates heat. Increasing the screw speed and/or screw diameter to achieve a higher output rate in a single-screw extruder will therefore result in a higher buildup of frictional heat and higher temperatures. In contrast, in twin-screw extruders with intermeshing screws the relative motion of the flight of one screw inside the channel of the other pushes the material forward almost as if the machine were a positive-displacement gear pump which conveys the material with very low friction.

In two-screw extruders, heat is therefore controlled independently from an outside source and is not influenced by screw speed. This fact becomes especially important when processing a heat-sensitive plastic like poly(vinyl chloride) (PVC). Multiple-screw extruders are therefore gaining wide acceptance for processing vinyls, although they are more expensive than single-screw machines. For the same reason, multiple-screw extruders have found a major use in the production of high-quality rigid PVC pipe of large diameter.

Several types of multiple-screw machines are available, including intermeshing corotating screws (in which the screws rotate in the same direction, and the flight of one screw moves inside the channel of the other), intermeshing counterrotating screws (in which the screws rotate in opposite directions), and nonintermeshing counterrotating screws.

Multiple-screw extruders can involve either two screws (twin-screw design) or four screws. A typical four-screw extruder is a two-stage machine, in which a twin-screw plasticating section feeds into a twin-screw discharge section located directly below it. The multiple screws are generally sized on output rates (lb/h) rather than on L/D ratios or barrel diameters.

2.7.4 Blown-Film Extrusion

The blown-film technique is widely used in the manufacture of polyethylene and other plastic films [14,15]. A typical setup is shown in [Figure 2.23](#). In this case the molten polymer from the extruder head enters the die, where it flows round a mandrel and emerges through a ring-shaped opening in the form of a tube. The tube is expanded into a bubble of the required diameter by the pressure of internal air admitted through the center of the mandrel. The air contained in the bubble cannot escape because it is sealed by the die at one end and by the nip (or pinch) rolls at the other, so it acts like a permanent shaping mandrel once it has been injected. An even pressure of air is maintained to ensure uniform thickness of the film bubble.

The film bubble is cooled below the softening point of the polymer by blowing air on it from a cooling ring placed round the die. When the polymer, such as polyethylene, cools below the softening point, the crystalline material is cloudy compared with the clear amorphous melt. The transition line which coincides with this transformation is therefore called the frost line.

The ratio of bubble diameter to die diameter is called the blowup ratio. It may range as high as 4 or 5, but 2.5 is a more typical figure. Molecular orientation occurs in the film in the hoop direction during blowup, and orientation in the machine direction, that is, in the direction of the extrudate flow from the die, can be induced by tension from the pinch rolls. The film bubble after solidification (at frost line) moves upward through guiding devices into a set of pinch rolls which flatten it. It can then be slit, gusseted, and surface-treated in line. (Vertical extrusion, shown in [Figure 2.23](#), is most common, although horizontal techniques have been successfully used.)

Blown-film extrusion is an extremely complex subject, and a number of problems are associated with the production of good-quality film. Among the likely defects are variation in film thickness, surface

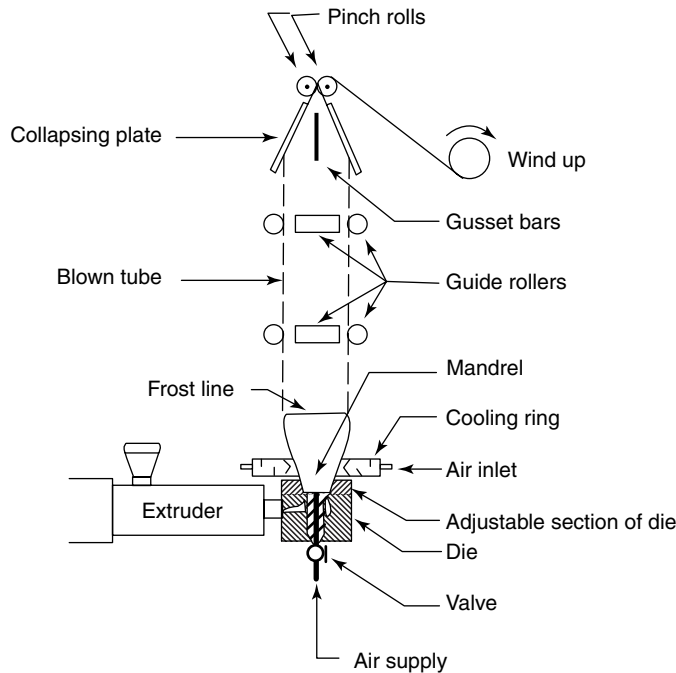


FIGURE 2.23 Typical blow-film extrusion setup.

imperfections (such as “fish eyes,” “orange peel,” haze), wrinkling, and low tensile strength. The factors affecting them are also numerous. “Fish eyes” occur due to imperfect mixing in the extruder or due to contamination of the molten polymer. Both factors are controlled by the screen pack.

The blown-film technique has several advantages: the relative ease of changing film width and caliber by controlling the volume of air in the bubble and the speed of the screw; the elimination of the end effects (e.g., edge bead trim and nonuniform temperature that result from flat film extrusion); and the capability of biaxial orientation (i.e., orientation both in the hoop direction and in the machine direction), which results in nearly equal physical properties in both directions, thereby giving a film of maximum toughness.

After extrusion, blown-film is often slit and wound up as flat film, which is often much wider than anything produced by slot-die extrusion. Thus, blown-films of diameters 7 ft. or more have been produced, giving flat film of widths up to 24 ft. One example is reported [16] of a 10-in. extruder with 5-ft diameter and a blowup ratio of 2.5, producing 1,100 lb/h, or polyethylene film, which when collapsed and slit in 40 ft wide. Films in thicknesses of 0.004–0.008 in. are readily produced by the blown-film process. Polyethylene films of such large widths and small thicknesses find extensive uses in agriculture, horticulture, and building.

2.7.5 Flat Film or Sheet Extrusion

In the flat-film process the polymer melt is extruded through a slot die (T-shaped or “coat hanger” die), which may be as wide as 10 ft. The die has relatively thick wall sections on the final lands (as compared to the extrusion coating die) to minimize deflection of the lips from internal melt pressure. The die opening (for polyethylene) may be 0.015–0.030 in.—even for films that are less than 0.003 in. thick. The reason is that the speed of various driven rolls used for taking up the film is high enough to draw down the film with a concurrent thinning. (By definition, the term *film* is used for material less than 0.010 in. thick, and *sheet* for that which is thicker.)

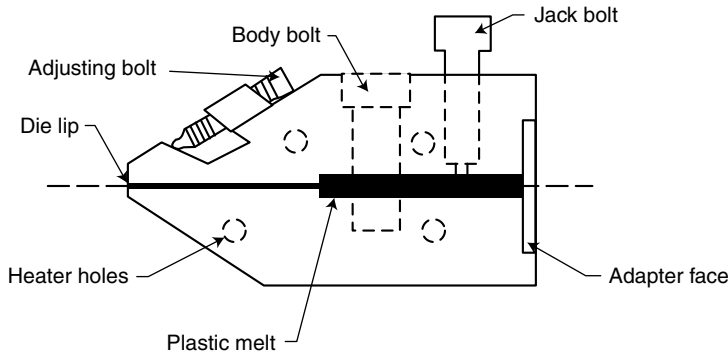


FIGURE 2.24 Sheet extrusion die.

Figure 2.24 illustrates the basic components of a sheet extrusion die. The die is built in two halves the part for easier construction and maintenance. The use of a jack bolt facilitates separation of the die halves when the die is full of plastic. The die lip can be adjusted (across the entire lip length) to enable the processor to keep the thickness of the extruded sheet within specification.

Figure 2.25 illustrates a T-type die and a coat-hanger-type die, which are used for both film and sheet extrusion. The die must produce a smooth and uniform laminar flow of the plastic melt which has already been mixed thoroughly in the extruder. The internal shape of the die and the smoothness of the die surface are critical to this flow transition. The deckle rods illustrated in Figure 2.25 are used by the processor to adjust the width of the extruded sheet or film.

Following extrusion, the film may be chilled below T_m or T_g by passing in through a water bath or over two or more chrome-plated chill rollers which have been cored for water cooling. A schematic drawing of a chill-roll (also called cast-film) operation is shown in Figure 2.26. The polymer melt extruded as a web from the die is made dimensionally stable by contacting several chill rolls before being pulled by the powered carrier rolls and wound up. The chrome-plated surface of the first roll is highly polished so that the product obtained is of extremely high gloss and clarity.

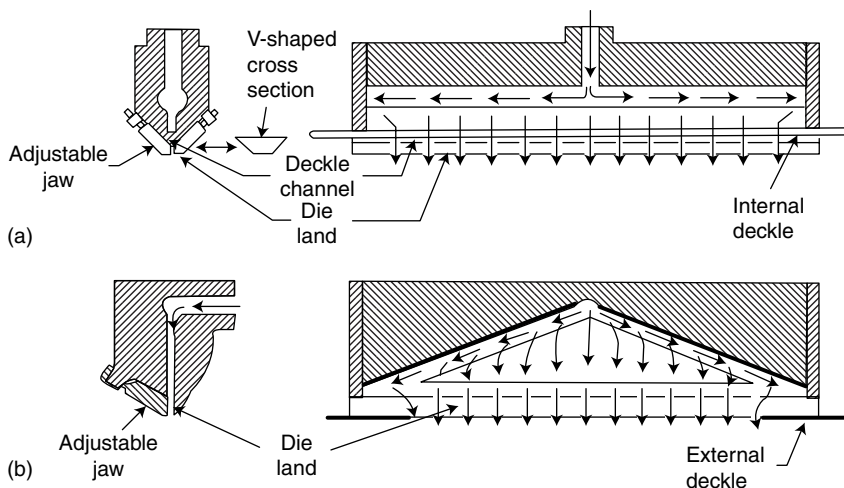


FIGURE 2.25 Schematic cross-sections (a) T-type and (b) coat-hanger-type extrusion dies.

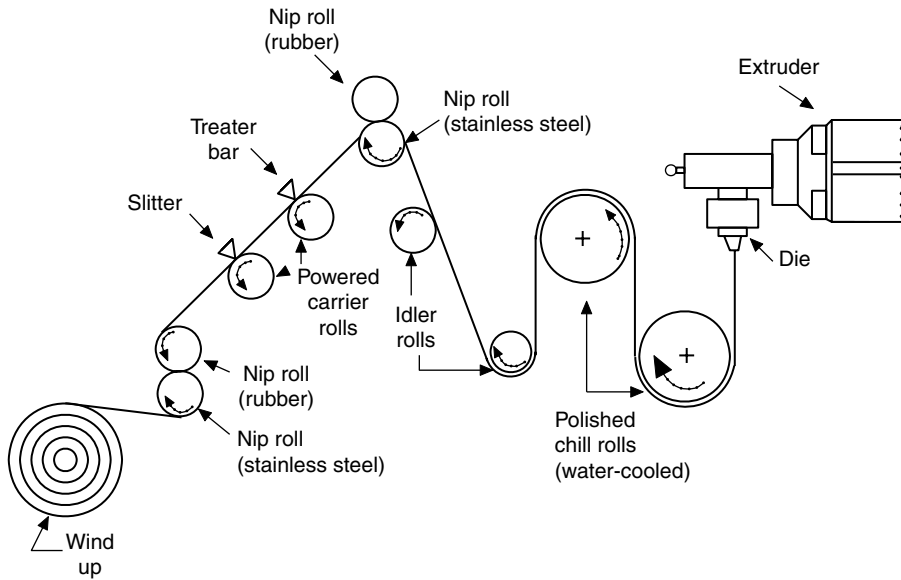


FIGURE 2.26 Sketch of chill-roll film extrusion. (After Lukov, L. J. 1963. *SPE J.*, 13, 10, 1057.)

In flat-film extrusion (particularly at high takeoff rates), there is a relatively high orientation of the film in the machine direction (i.e., the direction of the extrudate flow) and a very low one in the traverse direction.

Biaxially oriented film can be produced by a flat-film extrusion by using a tenter (Figure 2.27). Polystyrene, for example, is first extruded through a slit die at about 190°C and cooled to about 120°C by passing between rolls. Inside a temperature-controlled box and moving sheet, rewarmed to 130°C, is grasped on either side by tenterhooks which exert a drawing tension (longitudinal stretching) as well as widening tension (lateral stretching). Stretch ratios of 3:1–4:1 in both

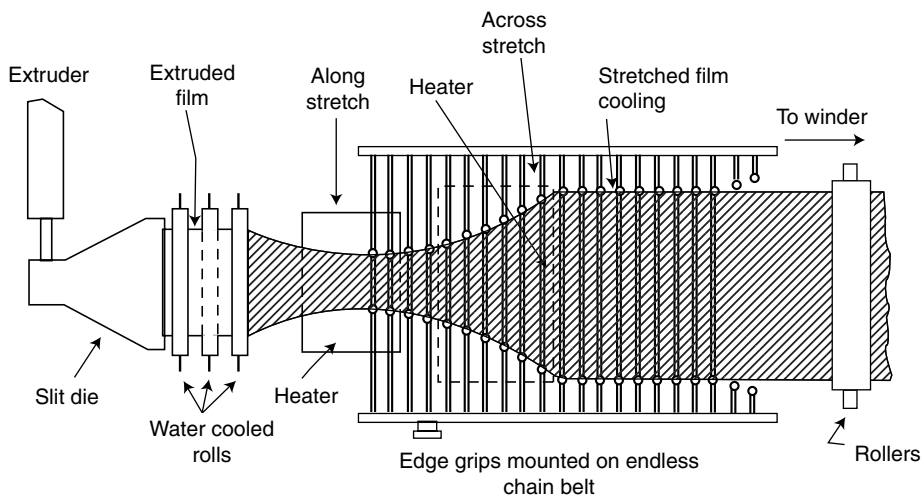


FIGURE 2.27 Plax process for manufacture of biaxially stretched polystyrene film.

directions are commonly employed for biaxially oriented polystyrene film. Biaxial stretching leads to polymers of improved tensile strength. Commercially available oriented polystyrene film has a tensile strength of 10,000–12,000 psi (703–843 kg/cm²), compared to 6,000–8,000 psi (422–562 kg/cm²) for unstretched material.

Biaxial orientation effects are important in the manufacture of films and sheet. Biaxially stretched polypropylene, poly(ethyleneterephthalate) (e.g., Melinex) and poly(vinylidene chloride) (Saran) produced by flat-film extrusion and tentering are strong films of high clarity. In biaxial orientation, molecules are randomly oriented in two dimensions just as fibers would be in a random mat; the orientation-induced crystallization produces structures which do not interfere with the light waves. With polyethylene, biaxial orientation often can be achieved in blown-film extrusion.

2.7.6 Pipe or Tube Extrusion

The die used for the extrusion of pipe or tubing consists of a die body with a tapered mandrel and an outer die ring which control the dimensions of the inner and outer diameters, respectively. Since this process involves thicker walls than are involved in blown-film extrusion, it is advantageous to cool the extrudate by circulating water through the mandrel (Figure 2.28) as well as by running the extrudate through a water bath.

The extrusion of rubber tubing, however, differs from thermoplastic tubing. For thermoplastic tubing, dimensional stability results from cooling below T_g or T_m , but rubber tubing gains dimensional stability due to a cross-linking reaction at a temperature above that in the extruder. The high melt viscosity of the rubber being extruded ensures a constant shape during the cross-linking.

A complication encountered in the extrusion of continuous shapes is die swell. Die swell is the swelling of the polymer when the elastic energy stored in capillary flow is relaxed on leaving the die. The extrusion of flat sheet or pipe is not sensitive to die swell, since the shape remains symmetrical even through the dimensions of the extrudate differ from those of the die. Unsymmetrical cross sections may, however, be distorted.

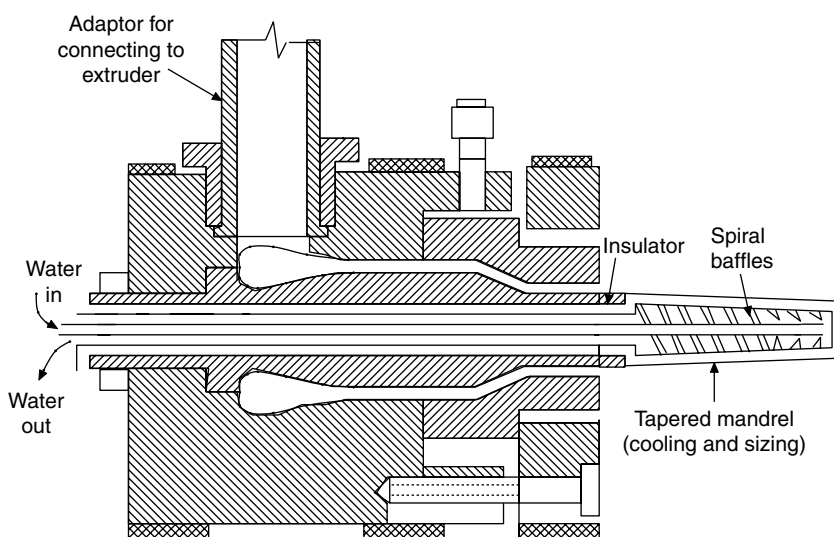


FIGURE 2.28 An extrusion die fitted with a tapered cooling and sizing mandrel for use in producing either pipe or tubing. (After Fisher, E. G. 1971. *Blow Molding of Plastics*. Iliffe, London.)

2.7.7 Wire and Cable Coverings

The covering or coating of wire and cable in continuous lengths with insulating plastics is an important application of extrusion, and large quantities of resin are used annually for this purpose. This applications represented one of the first uses of extruders for rubber about 100 years ago. The wire and cable coating process resembles the process used for pipe extrusion (Figure 2.28) with the difference that the conductor (which may be a single metal strand, a multiple strand, or even a bundle of previously individually insulated wires) to be covered is drawn through the mandrel on a continuous basis (Figure 2.29). For thermoplastics such as polyethylene, nylon, and plasticized PVC, the coating is hardened by cooling below T_m or T_g by passing through a water trough. Rubber coatings, on the other hand, are to be cross-linked by heating subsequent to extrusion.

2.7.8 Extrusion Coating

Many substrates, including paper, paperboard, cellulose film, fireboard, metal foils, or transparent films are coated with resins by direct extrusion. The resins most commonly used are the polyolefins, such as polyethylene, polypropylene, ionomer, and ethylene–vinyl acetate copolymers. Nylon, PVC, and polyester are used for a lesser extent. Often combinations of these resins and substrates are used to provide a multiplayer structure. [A related technique, called extrusion laminating, involves two or more substrates, such as paper and aluminum foil, combined by using a plastic film, (e.g., polyethylene) as the adhesive and as a moisture barrier.] Coatings are applied in thicknesses of about 0.2–15 mils, the common average being 0.5–2 mils, and the substrates range in thickness from 0.5 to more than 24 mils.

The equipment used for extrusion coating is similar to that used for the extrusion of flat film. Figure 2.30 shows a typical extrusion coating setup. The thin molten film from the extruder is pulled down into the nip between a chill roll and a pressure roll situated directly below the die. The pressure between these two rolls forces the film on to the substrate while the substrate, moving at a speed faster than the extruded film, draws the film to the required thickness. The molten film is cooled by the water-cooled, chromium-plated chill roll. The pressure roll is also metallic but is covered with a rubber sleeve, usually neoprene or silicone rubber. After trimming, the coated material is wound up on conventional windup equipment.

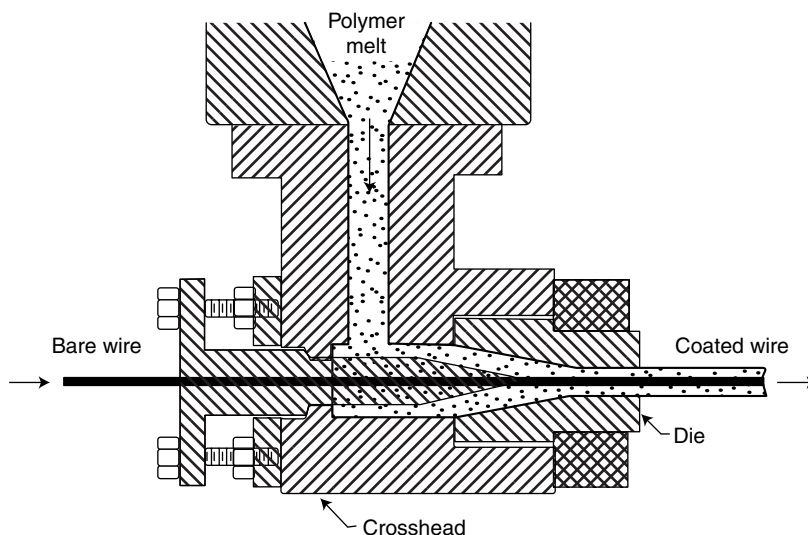


FIGURE 2.29 Crosshead used for wire coating.

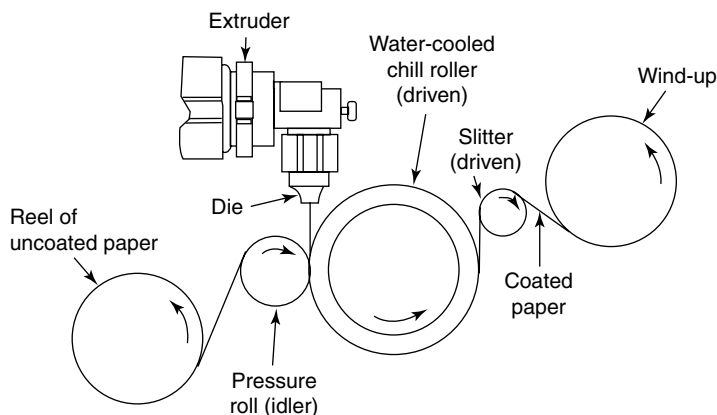


FIGURE 2.30 Sketch of paper coating for extrusion process.

2.7.9 Profile Extrusion

Profile extrusion is similar to pipe extrusion (Figure 2.28) except that the sizing mandrel is obviously not necessary. A die plate, in which an orifice of appropriate geometry has been cut, is placed on the face of the normal die assembly. The molten polymer is subjected to surface drag as it passes through the die, resulting in reduced flow through the thinner sections of the orifice. This effect is countered by altering the shape of the orifice, but often this results in a wide difference in the orifice shape from the desired extrusion profile. Some examples are shown in Figure 2.31.

2.8 Blow Molding

Basically, blow molding is intended for use in manufacturing hollow plastic products, such as bottles and other containers [17]. However, the process is also used for the production of toys, automobile parts, accessories, and many engineering components. The principles used in blow molding are essentially similar to those used in the production of glass bottles. Although there are considerable differences in the process available for blow molding, the basic steps are the same: (1) melt the plastic; (2) form the molten plastic into a *parison* (a tubelike shape of molten plastic); (3) seal the ends of the parison except for one area through which the blowing air can enter; (4) inflate the parison to assume the shape of the mold in which it is placed; (5) cool the blow-molded part; (6) eject the blow-molded part; (7) trim flash if necessary.

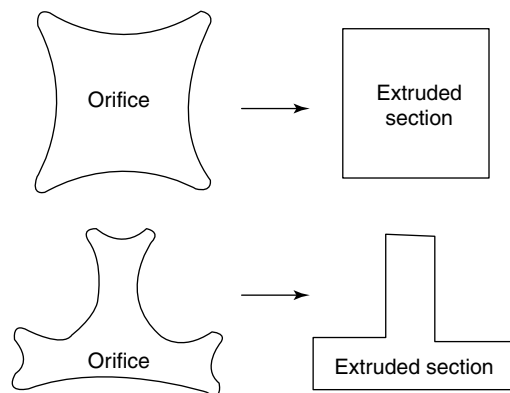


FIGURE 2.31 Relationships between extruder die orifice and extruded section.

Two basic processes of blow molding are extrusion blow molding and injection blow molding. These processes differ in the way in which the parison is made. The extrusion process utilizes an unsupported parison, whereas the injection process utilizes a parison supported on a metal core. The extrusion blow-molding process by far accounts for the largest percentage of blow-molded objects produced today. The injection process is, however, gaining acceptance.

Although any thermoplastic can be blow-molded, polyethylene products made by this technique are predominant. Polyethylene squeeze bottles form a large percentage of all blow-molded products.

2.8.1 Extrusion Blow Molding

Extrusion blow molding consists basically of the extrusion of a predetermined length of parison (hollow tube of molten plastic) into a split die, which is then closed, sealing both ends of the parison. Compressed air is introduced (through a blowing tube) into the parison, which blows up to fit the internal contours of the mold. As the polymer surface meets the cold metal wall of the mold, it is cooled rapidly below T_g or T_m . When the product is dimensionally stable, the mold is opened, the product is ejected, a new parison is introduced, and the cycle is repeated. The process affords high production rates.

In continuous extrusion blow molding, a molten parison is produced continuously from a screw extruder. The molds are mounted and moved. In one instance the mold sets are carried on a rotating horizontal table (Figure 2.32a), in another on the periphery of a rotating vertical wheel (Figure 2.32b). Such rotary machines are best suited for long runs and large-volume applications.

In the ram extrusion method the parison is formed in a cyclic manner by forcing a charge out from an accumulated molten mass, as in the preplasticizer injection-molding machine. The transport arm cuts and holds the parison and lowers it into the waiting mold, where shaping under air pressure takes place (Figure 2.33).

A variation of the blow-extrusion process which is particularly suitable for heat-sensitive resins such as PVC is the cold perform molding. The parison is produced by normal extrusion and cooled and stored until needed. The required length of tubing is then reheated and blown to shape in a cold mold, as in conventional blow molding. Since, unlike in the conventional process, the extruder is not coupled directly to the blow-molding machine, there is less chance of a stoppage occurring, with consequent risk of holdup and degradation of the resin remaining in the extruder barrel. There is also less chance of the occurrence of “dead” pockets and consequent degradation of resin in the straight-through die used in this process than in the usual crosshead used with a conventional machine.

2.8.2 Injection Blow Molding

In this process the parison is injection molded rather than extruded. In one system, for example, the parison is formed as a thick-walled tube around a blowing stick in a conventional injection-molding machine. The parison is then transferred to a second, or blowing, mold in which the parison is inflated to the shape of the mold by passing compressed air down the blowing stick. The sequence is shown in

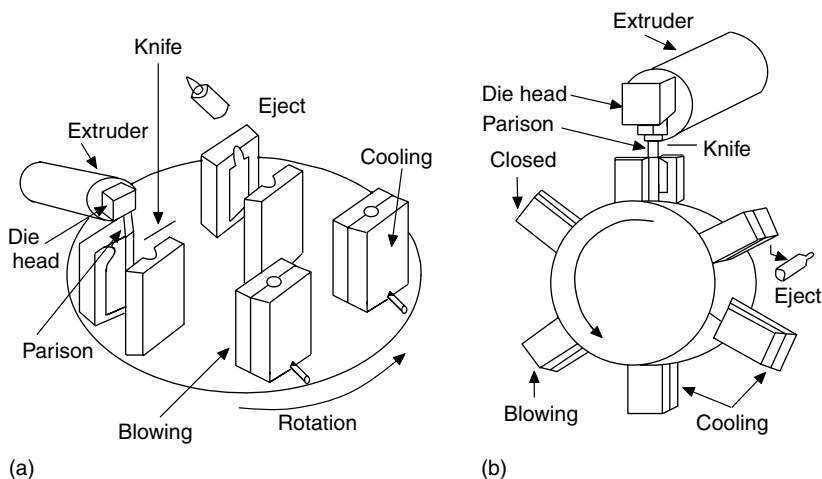


FIGURE 2.32 Continuous extrusion blow molding. (a) Rotating horizontal table carrying mold sets. (b) Continuous vertical rotation of a wheel carrying mold sets on the periphery. (After Frados, J. ed. 1976. *Plastics Engineering Handbook*, 4th Ed., Van Nostrand Reinhold, New York.)

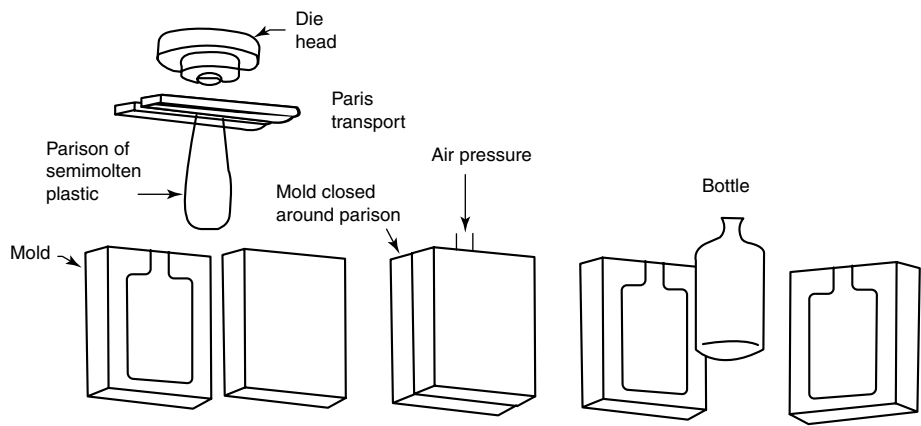


FIGURE 2.33 Continuous extrusion blow molding with parison transfer. The transport arm cuts the extruded parison from the die head and lowers it into the waiting mold.

Figure 2.34. Injection blow molding is relatively slow and is more restricted in choice of molding materials as compared to extrusion blow molding. The injection process, however, affords good control of neck and wall thicknesses of the molded object. With this process it is also easier to produce unsymmetrical molding.

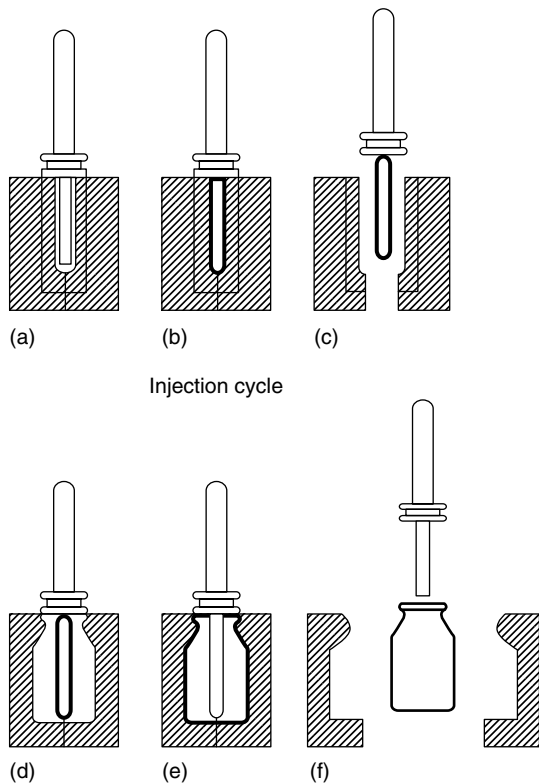


FIGURE 2.34 Sketch of injection-blow-molding process.

2.8.3 Blow Molds

Generally, the blow mold is a cavity representing the outside of a blow-molded part. The basic structure of a blow mold consists of a cast or machined block with a cavity, cooling system, venting system, pinchoffs, flash pockets, and mounting plate. The selection of material for the construction of a blow mold is based on the consideration of such factors as thermal conductivity, durability, cost of the material, the resin being processed, and the desired quality of the finished parts. Commonly used mold materials are beryllium, copper, aluminum, ampcoloy, A-2 steel, and 17-4 and 420 stainless steels.

Beryllium–copper (BeCu) alloys 165 and 25 are normally used for blow molds. These materials display medium to good thermal conductivity with good durability. Stainless steels such as 17-4 and 420 are also frequently employed in blow molds where durability and resistance to hydrochloric acid are required. Heat-treated A-2 steel is often used as an insert in pinchoffs where thermal conductivity is not a concern and high quality parts are required.

For blow molding HDPE parts, aluminum is commonly employed for the base material, with BeCu or stainless steel inserts in the pinchoff areas. For PVC parts BeCu, ampcoloy, or 17-4 stainless steel are used as the base material, with A-2 or stainless inserts in the pinchoff area. For PET parts, the base mold is typically made of aluminum or BeCu, with A-2 or stainless steel pinchoffs.

The production speed of blow-molded parts is generally limited by one of two factors: extruder capacity or cooling time in the mold. Cooling of mold is accomplished by a water circuit into the mold. Flood cooling and cast-in tubes are most common in cast molds; drilled holes and milled slots are the norm in machined blow molds.

In multiple-cavity molds, series and parallel cooling circuits are used. Series cooling enters and cools one cavity, then moves to the next until all the cavities are cooled. The temperature of the water increases as it moves through the mold, and this results in non-uniform cooling. Parallel cooling, on the other hand, enters and exists all cavities simultaneously, thereby cooling all cavities at a uniform rate. Parallel cooling is thus the preferred method but it is not always possible due to limitations.

2.9 Calendering

Calendering is the leading method for producing vinyl film, sheet, and coatings [18]. In this process continuous sheet is made by passing a heat-softened material between two or more rolls. Calendering was originally developed for processing rubber, but is now widely used for producing thermoplastic films, sheets, and coatings. A major portion of thermoplastics calendered is accounted for by flexible (plasticized) PVC. Most plasticized PVC film and sheet, ranging from the 3-mil film for baby pants to the 0.10 in “vinyl” tile for floor coverings, is calendered.

The calendaring process consists of feeding a softened mass into the nip between two rolls where it is squeezed into a sheet, which then passes round the remaining rolls. The processed material thus emerges as a continuous sheet, the thickness of which is governed by the gap between the last pair of rolls. The surface quality of the sheet develops on the last roll and may be glossy, matt, or embossed. After leaving the calender, the sheet is passed over a number of cooling rolls and then through a beta-ray thickness gage before being wound up.

The plastics mass fed to the calender may be simply a heat-softened material, as in the case of, say, polyethylene, or a rough sheet, as in the case of PVC. The polymer PVC is blended with stabilizers, plasticizers, etc., in ribbon blenders, gelated at 120°C–160°C for about 5–10 min in a Banbury mixer, and the gelated lumps are made into a rough sheet on a two-roll mill before being fed to the calender.

Calenders may consist of two, three, four, or five hollow rolls arranged for steam heating or water cooling and are characterized by the number of rolls and their arrangement. Some arrangements are shown in [Figure 2.35](#). Thick sections of rubber can be made by applying one layer of polymer upon a previous layer (double plying) ([Figure 2.35b](#)). Calenders can be used for applying rubber or plastics to fabrics ([Figure 2.35c](#)). Fabric or paper is fed through the last two rolls of the calender so that the resin film is pressed into the surface of the web. For profiling, the plastic material is fed to the nip of the calender,

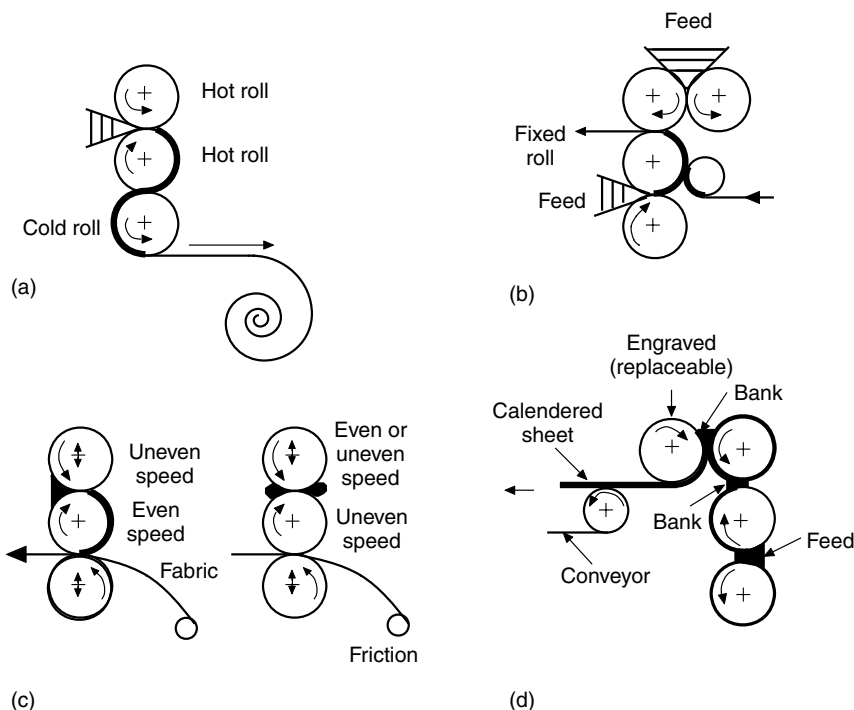


FIGURE 2.35 Typical arrangements of calender rolls: (a) single-ply sheeting; (b) double-ply sheeting; (c) applying rubber to fabrics; (d) profiling with four-roll engraving cylinder.

where the material assumes the form of a sheet, which is then progressively pulled through two subsequent banks to resurface each of the two sides (Figure 2.35d). For thermoplastics the cooling of the sheet can be accomplished on the rolls with good control over dimensions. For rubber, cross-linking can be carried out with good control over dimensions, with the support of the rolls. Despite the simple appearance of the calender compared to the extruder, the close tolerances involved and other mechanical problems make for the high cost of a calendaring unit.

2.10 Spinning of Fibers

The term spinning, as used with natural fibers, refers to the twisting of short fibers into continuous lengths [19–21]. In the modern synthetic fiber industry, however, the term is used for any process of producing continuous lengths by any means. (A few other terms used in the fiber industry should also be defined. A fiber may be defined as a unit of matter having a length at least 100 times its width or diameter. An individual strand of continuous length is called a filament. Twisting together filaments into a strand gives continuous filament yarn. If the filaments are assembled in a loose bundle, we have tow or roving. These can be chopped into small lengths (an inch to several inches long), referred to as staple. Spun yarn is made by twisting lengths of staple into a single continuous strand, and *cord* is formed by twisting together two or more yarns.)

The dimensions of a filament or yarn are expressed in terms of a unit called the “tex” which is a measure of the fineness or linear density. One tex is 1 gram per 1,000 meters or 10^{-6} kg/m. The tex has replaced “denier” as a measure of the density of the fiber. One denier is 1 gram per 9,000 meters, so 1 denier = 0.1111 tex.

The primary fabrication process in the production of synthetic fibers is the spinning—i.e., the formation—of filaments. In every case the polymer is either melted or dissolved in a solvent and is put in filament form by forcing through a die, called spinneret, having a multiplicity of holes. Spinnerets for rayon spinning, for example, have as many as 10,000 holes in a 15-cm-diameter platinum disc, and those for textile yarns may have 10–120 holes; industrial yarns such as tire core might be spun from spinnerets with up to 720 holes.

Three major categories of spinning processes are melt, dry, and wet spinning [19]. The features of the three processes are shown in Figure 2.36, and the typical cross sections of the fibers produced by them are shown in Figure 2.37.

2.10.1 Melt Spinning

In melt spinning, which is the same as melt extrusion, the polymer is heated and the viscous melt is pumped through a spinneret. An inert atmosphere is provided in the melting chamber before the pump. Special pumps are used to operate in the temperature range necessary to produce a manageable melt (230–315°C). For nylon, for example, a gear pump is used to feed the melt to the spinneret (Figure 2.36a). For a polymer with high melt viscosity such as polypropylene, a screw extruder is used to feed a heated spinneret. Dimensional stability of the fiber is obtained by cooling under tension.

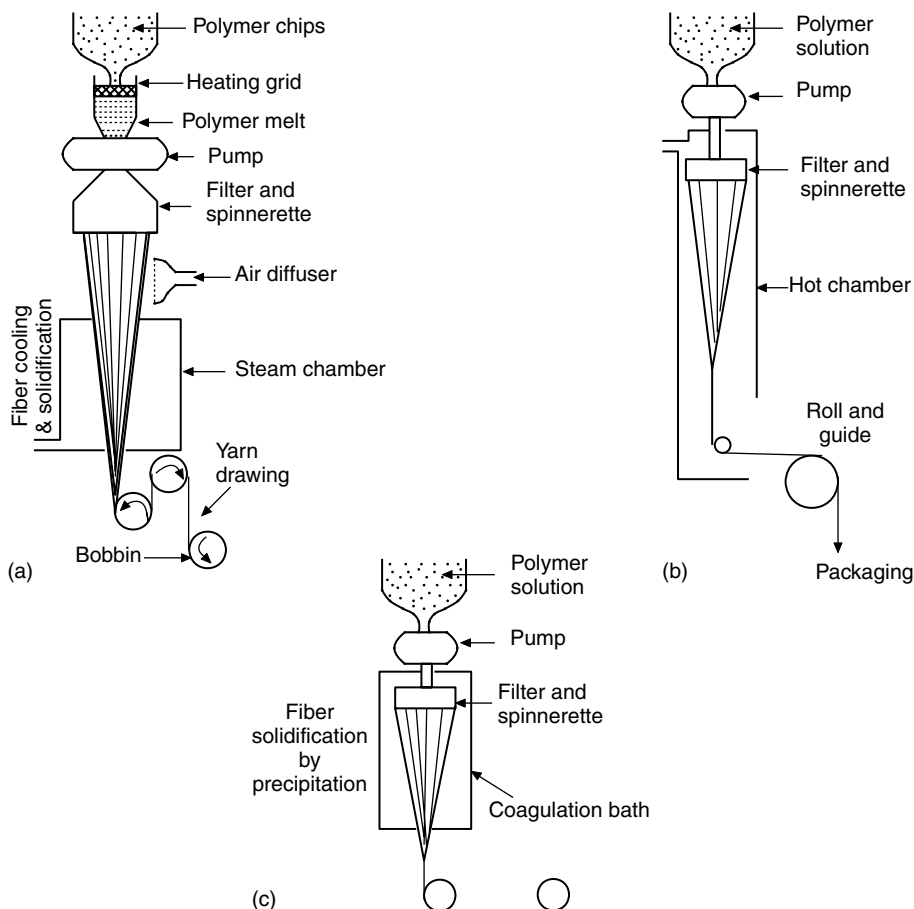


FIGURE 2.36 Schematic of the three principal types of fiber spinning: (a) melt spinning; (b) dry spinning; (c) wet spinning. (After Carraher, C. E., Jr. 2002. *Polymer News*, 27, 3, 91.)

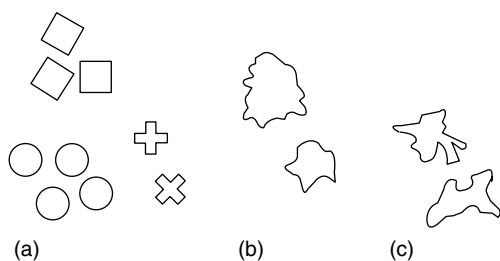


FIGURE 2.37 Typical cross-section of fibers produced by different spinning processes: (a) melt-spun nylon from various shaped orifices; (b) dry-spun cellulose acetate from round orifice; (c) wet-spun viscose rayon from round orifice.

Typical melt spinning temperatures are given in [Table 2.1](#).

2.10.2 Dry Spinning

In dry spinning, a polymer is dissolved in a solvent and the polymer solution (concentration on the order of 20–40%) is filtered and then forced through a spinneret into a chamber through which heated air is passed to achieve dimensional stability of the fiber by evaporation of the solvent ([Figure 2.36b](#)). For economical reasons, the gas is usually air, but inert gases such as nitrogen and superheated steam are sometimes used. The skin which forms first on the fiber by evaporation from the surface gradually collapses and wrinkles as more solvent diffuses out and the diameter

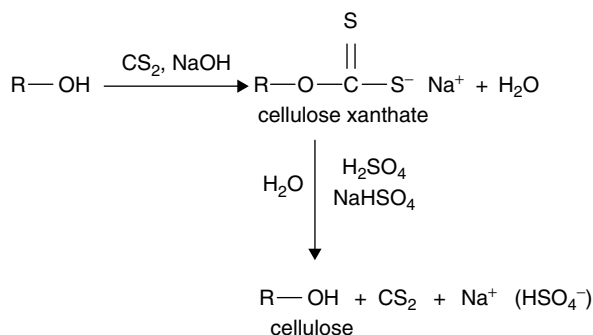
decreases. The cross section of a dry-spun fiber thus has an irregularly lobed appearance ([Figure 2.37](#)). Recovery of the solvent used for dissolving the polymer is important to the economics of the process. Cellulose acetate dissolved in acetone and polyacrylonitrile (PAN) dissolved in dimethylformamide are two typical examples.

The hot solution (dope) of PAN in DMF is extruded directly into a hot stream of nitrogen at 300°C. The residual DMF is recovered in subsequent water washing steps.

Dry spun fibers have lower void concentrations than wet spun fibers. This is reflected in greater densities and lower dyeability for the dry spun fibers.

2.10.3 Wet Spinning

Wet spinning also involves pumping a solution of the polymer to the spinneret. However, unlike dry spinning, dimensional stability is achieved by precipitating the polymer in a nonsolvent ([Figure 2.36c](#)). For example, PAN in dimethylformamide can be precipitated by passing a jet of the solution through a bath of water, which is miscible with the solvent but coagulates the polymer. For wet-spinning cellulose triacetate a mixture methylene chloride and alcohol can be used to dissolve the polymer, and a toluene bath can be used for precipitation of the polymer. In some cases the precipitation can also involve a chemical reaction. An important example is viscose rayon, which, is made by regenerating cellulose from a solution of cellulose xanthate in dilute alkali.



If a slot die rather than a spinneret is used, the foregoing process would yield cellulose film (cellophane) instead of fiber.

TABLE 2.1 Typical Spinning Temperatures for Selected Polymers

Polymer	Melting Point (°C)	Typical Spinning Temperature (°C)
Nylon-6	220	280
Nylon-6,6	260	290
Poly(ethylene terephthalate)	260	290
Polyethylene	~ 130	220–230
Polypropylene	170	250–300
Poly(vinylidene chloride) copolymers	120–140	180

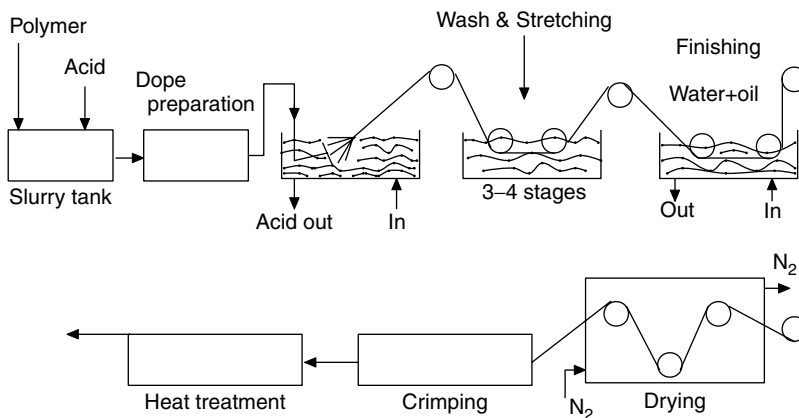
Source: Carraher, C. E. Jr. 2002. *Polymer News*, 27(3), 91.

Wet spinning is the most complex of the three spinning processes, typically including washing, stretching, drying, crimping, finish application, and controlled relaxation to form tow material [22]. A simplified sketch of the Asahi wet spinning process for making PAN (acrylic) fiber tows is shown in Figure 2.38. The polymer solution (dope) is made in concentrated HNO_3 (67%) at low temperatures using pulverizer and mixer, filtered, and deaerated. The dope, containing 14–15% polymer and maintained at -7°C , is extruded at a pumping pressure of 10–15 atm through the spinnerets immersed in the coagulation bath. Each spinneret has about 46,000–73,000 holes (different sizes for different grades). The acid concentration in the bath is 37% and the temperature is -5°C . The filaments from 5 spinnerets are collected into a tow. The spinning speed in this step is about 7 meters per minute. The dilute nitric acid from the bath goes to the concentration section where 67% HNO_3 is obtained for re-use in dope preparation.

In the next pre-finishing step, the fibers (tows) are repeatedly washed with water by spraying and immersion to remove the acid. The fiber is stretched in three stages, a 1:10 stretch being obtained in the last hot water bath at 100°C . In the finishing section, the tows pass through a water bath containing 1% oil to impart antistaticity and reduce friction. The tows are then dried in a hot air (135°C) dryer over rollers. Subsequent treatments include a second finishing oil spray, crimping, second hot air drying, plaiting, thermosetting, and cutting into staple fibers.

Fibers made from wet spinning generally have high void contents in comparison to all of the other processes giving them increased dyeability and the surface is rougher with longitudinal serrations.

Hollow fibers for gas and liquid separation are prepared by passing air through the material just prior to entrance into the non-solvent bath.

**FIGURE 2.38** A simplified sketch of the Asahi wet spinning process for polyacrylonitrile fiber.

2.10.4 Cold Drawing of Fibers

Almost all synthetic fibers are subjected to a drawing (stretching) operation to orient the crystalline structure in the direction of the fiber axis. Drawing orients crystallites in the direction of the stretch so that the modulus in that direction is increased and elongation at break is decreased. Usually the drawing is carried out at a temperature between T_g and T_m of the fiber. Thus, polyethylene ($T_g = -115^\circ\text{C}$) can be drawn at room temperature, whereas nylon-6,6 ($T_g = 53^\circ\text{C}$) should be heated or humidified to be drawn. T_g is depressed by the presence of moisture, which acts as a plasticizer. The drawing is accomplished by winding the yarn around a wheel or drum driven at a faster surface velocity than a preceding one.

2.11 Thermoforming

When heated, thermoplastic sheet becomes as soft as a sheet of rubber, and it can then be stretched to any given shape [23]. This principle is utilized in thermoforming processes which may be divided into three main types: (a) vacuum forming, (2) pressure forming (blow forming), and (3) mechanical forming (e.g., matched metal forming), depending on the means used to stretch the heat softened sheet.

Since fully cured thermoset sheets cannot be resoftened, forming is not applicable to them. Common materials subjected to thermoforming are thermoplastics such as polystyrene, cellulose acetate, cellulose acetate butyrate, PVC, ABS, poly(methyl methacrylate), low- and high-density polyethylene, and polypropylene. The bulk of the forming is done with extruded sheets, although cast, calendered, or laminated sheets can also be formed.

In general, thermoforming techniques are best suited for producing moldings of large area and very thin-walled moldings, or where only short runs are required. Thermoformed articles include refrigerator and freezer door liners complete with formed-in compartments for eggs, butter, and bottles of various types, television masks, dishwasher housings, washing machine covers, various automobile parts (instrument panels, arm rests, ceilings, and door panels), large patterned diffusers in the lighting industry, displays in advertising, various parts in aircraft industry (windshields, interior panels, arm rests, serving trays, etc.), various housing (typewriters, Dictaphones, and duplicating machines), toys, transparent packages, and much more.

2.11.1 Vacuum Forming

In vacuum forming, the thermoplastic sheet can be clamped or simply held against the RIM of a mold and then heated until it becomes soft. The soft sheet is then sealed at the RIM, and the air from the mold cavity is removed by a suction pump so that the sheet is forced to take the contours of the mold by the atmospheric pressure above the sheet (Figure 2.39a). The vacuum in the mold cavity is maintained until the part cools and becomes rigid.

Straight cavity forming is not well adapted to forming a cup or box shape because as the sheet, drawn by vacuum, continues to fill out the mold and solidify, most of the stock is used up before it reaches the periphery of the base, with the result that this part becomes relatively thin and weak. This difficulty is alleviated and uniformity of distribution in such shapes is promoted if the *plug assist* is used (Figure 2.39b). The plug assist is any type of mechanical helper which carries extra stock toward an area where the part would otherwise be too thin.

Plug-assist techniques are adaptable both to vacuum-forming and pressure forming techniques. The system shown in Figure 2.39b is thus known as plug assist vacuum forming.

2.11.2 Pressure Forming

Pressure forming is the reverse of vacuum forming. The plastic sheet is clamped, heated until it becomes soft, and sealed between a pressure head and the RIM of a mold. By applying air pressure (Figure 2.40),

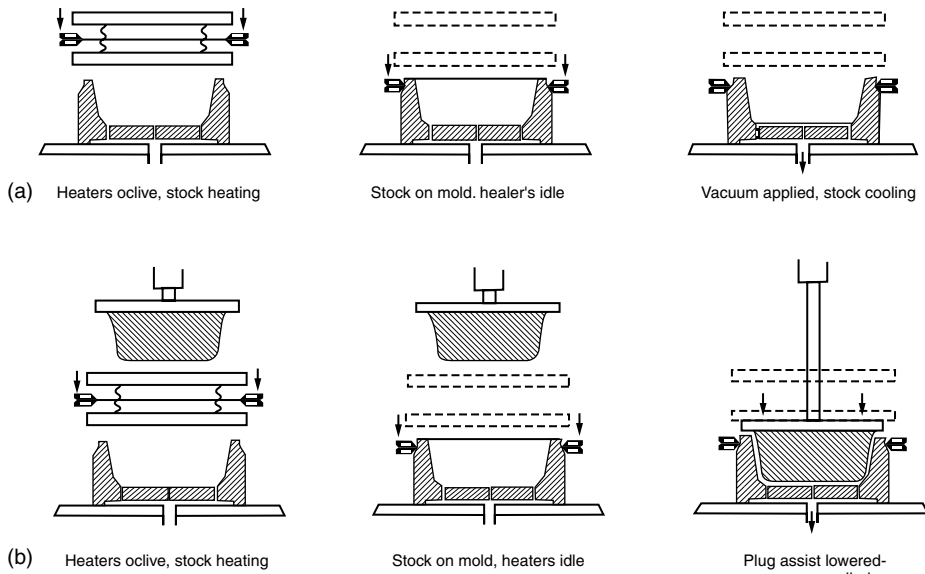


FIGURE 2.39 (a) Vacuum forming. (b) Plug-assist forming using vacuum.

one forces the sheet to take the contours of the mold. Exhaust holes in the mold allow the trapped air to escape. After the part cools and becomes rigid, the pressure is released and the part is removed. As compared to vacuum forming, pressure forming affords a faster production cycle, greater part definition, and greater dimensional control.

A variation of vacuum forming or pressure forming, called free forming or free blowing, is used with acrylic sheeting to produce parts that require superior optical quality (e.g., aircraft canopies). In this process the periphery is defined mechanically by clamping, but no mold is used, and the depth of draw or height is governed only by the vacuum or compressed air applied.

2.11.3 Mechanical Forming

Various mechanical techniques have been developed for thermoforming that use neither air pressure nor vacuum. Typical of these is matched mold forming (Figure 2.41). A male mold is mounted on

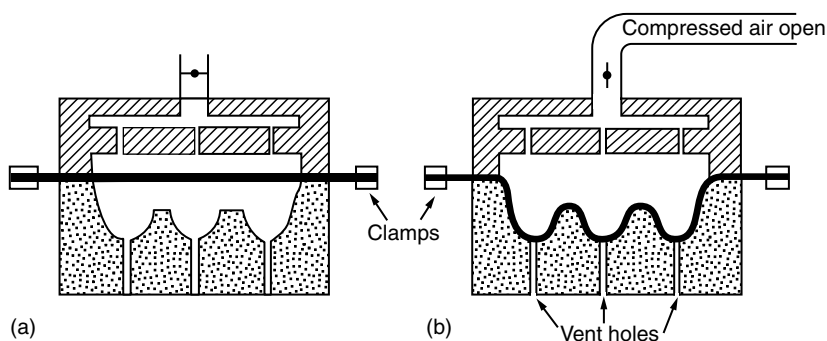


FIGURE 2.40 Pressure forming: (a) heated sheet is clamped over mold cavity; (b) compressed air pressure forces the sheet into the mold.

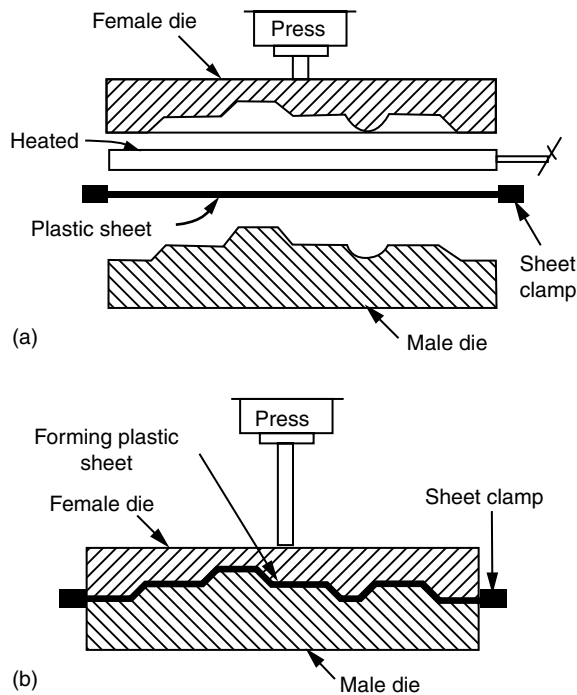


FIGURE 2.41 Matched mold forming: (a) heating; (b) forming.

the top or bottom platen, and a matched female mold is mounted on the other. The plastic sheet, held by a clamping frame, is heated to the proper forming temperature, and the mold is then closed, forcing the plastic to the contours of both the male and the female molds. The molds are held in place until the plastic cools and attains dimensional stability, the latter facilitated by internal cooling of the mold. The matched mold technique affords excellent reproduction of mold detail and dimensional accuracy.

2.12 Casting Processes

There are two basic types of casting used in plastics industry: simple casting and plastisol casting.

2.12.1 Simple Casting

In simple casting, the liquid is simply poured into the mold without applying any force and allowed to solidify. Catalysts that cause the liquid to set are often added. The resin can be a natural liquid or a granular solid liquefied by heat. After the liquid resin is poured into the closed mold, the air bubbles are removed and the resin is allowed to cure either at room temperature or in an oven at low heat. When completely cured, the mold is split apart and the finished casting is removed. In the production of simple shapes such as rods, tubes, etc., usually two-piece metal mold with an entry hole for pouring in the liquid resin is used. For making flat-cast acrylic plexiglass or lucite sheets, two pieces of polished plate glass separated by a gasket with the edge sealed and one corner open are usually used as a mold.

Both thermosets and thermoplastics may be cast. Acrylics, polystyrene, polyesters, phenolics, and epoxies are commonly used for casting.

2.12.2 Plastisol Casting

Plastisol casting, commonly used to manufacture hollow articles, is based on the fact that plastisol in fluid form is solidified as it comes in contact with a heated surface [24]. A plastisol is a suspension of PVC in a liquid plasticizer to produce a fluid mixture that may range in viscosity from a pourable liquid to a heavy paste. This fluid may be sprayed onto a surface, poured into a mold, spread onto a substrate, etc.

The plastisol is converted to a homogeneous solid (“vinyl”) product through exposure to heat [e.g., 350°F (176°C)], depending on the resin type and plasticizer type and level. The heat causes the suspended resin to undergo fusion—that is, dissolution in the plasticizer (Figure 2.42)—so that on cooling, a flexible vinyl product is formed with little or no shrinkage. The product possesses all the excellent qualities of vinyl plastics.

Dispersion-grade PVC resins are used in plastisols. These resins are of fine particle size (0.1–2 μm in diameter), as compared to suspension type resins (commonly 75–200 μm in diameter) used in calender and extrusion processing. A plastisol is formed by simply mixing the dispersion-grade resin into the plasticizer with sufficient shearing action to ensure a reasonable dispersion of the resin particles. (PVC plasticizers are usually monomeric phthalate esters, the most important of them being the octyl esters based on 2-ethylhexyl alcohol and isooctyl alcohol, namely dioctyl phthalate and diisooctyl phthalate, respectively.) The ease with which virtually all plastisol resins mix with plasticizer to form a smooth stable dispersion/paste is due to the fine particle size and the emulsifier coating on the resin particles. (The emulsifier coating aids the wetting of each particle by the plasticizer phase.)

The liquid nature of the plastisol system is the key to its ready application. The plastisol may be spread onto a cloth, paper, or metal substrate, or otherwise cast or slushed into a mold. After coating or molding, heat is applied, which causes the PVC resin particles to dissolve in the plasticizer and form a cohesive mass, which is, in effect, a solid solution of polymer in plasticizer.

The various changes a plastisol system goes through in the transformation from a liquid dispersion to a homogeneous solid are schematically shown in Figure 2.42. At 280°F (138°C) the molecules of plasticizer begin to enter between the polymer units, and fusion begins. If the plastisol were cooled after being brought to this temperature, it would give a cohesive mass with a minimum of physical strength. Full fusion occurs and full strength is accomplished when the plastisol is brought to approximately 325°F (163°C) before cooling. The optimum fusion temperature, however, depends on resin type and plasticizer type.

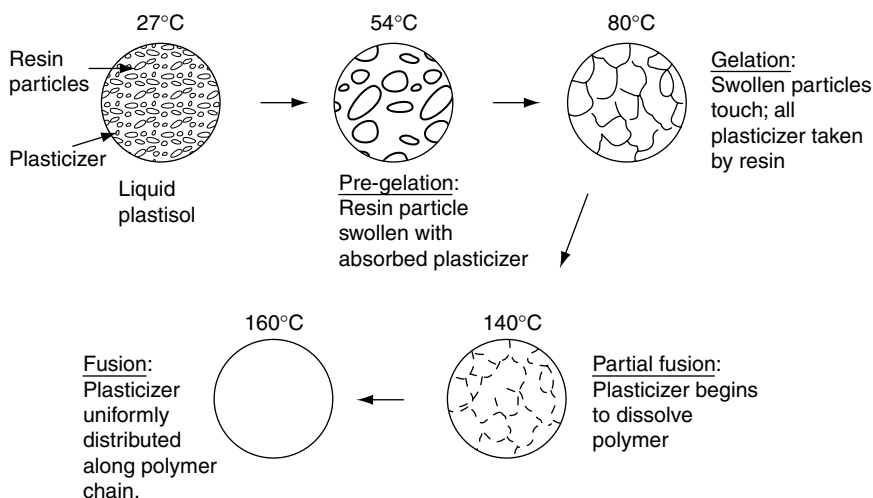


FIGURE 2.42 Various changes in a plastisol system in the transformation from a liquid dispersion to a homogenous solid.

For coating applications it is common practice to add solvent (diluent) to a plastisol to bring down viscosity. This mixture is referred to as organosol. It may be applied by various coating methods to form a film on a substrate and then is heated to bring about fusion, as in the case of plastisol.

Unlike coating applications, there are some applications where it is desirable to have an infinite viscosity at low shear stress. For such applications, a plastisol can be gelled by adding a metallic soap (such as aluminum stearate) or finely divided filler as a gelling agent to produce a plastigel. A plastigel can be cold molded, placed on a pan, and heated to fusion without flow. The whole operation is like baking cookies.

A rigidsol is a plastisol of such formulation that it becomes a rigid, rather than a flexible, solid when fused. A very rigid product can be obtained when the plasticizer is polymerized during or right after fusion. For example, a rigidsol can be made from 100 parts of PVC resin, 100 parts of triethylene glycol dimethacrylate (network forming plasticizer) and 1 part of di-*tert*-butyl peroxide (initiator). This mixture has a viscosity of only 3 poises compared with 25 poises for phthalate-based plastisol. However, after being heated for 10 min at 350°F (176°C), the resin solvates and the plasticizer polymerizes to a network structure, forming a hard, rigid glassy solid with a flexural modulus of over 2.5×10^5 psi (1.76×10^4 kg/cm²) at room temperature.

Three important variations of the plastisol casting, are dip casting, slush casting, and rotational casting.

2.12.2.1 Dip Casting

A heated mold is dipped into liquid plastisol (Figure 2.43a) and then drawn at a given rate. The solidified plastisol (with mold) is then cured in an oven at 350°F–400°F (176°C–204°C). After a cools, the plastic is stripped from the mold. Items with intricate shapes such as transparent ladies' overshoes, flexible gloves, etc., can be made by this process.

The dipping process is also used for coating metal objects with vinyl plastic. For example, wire dish drainers, coat hangers, and other industrial and household metal items can be coated with a thick layer of flexible vinyl plastic by simply dipping in plastisol and applying fusion.

2.12.2.2 Slush Casting

Slush casting is similar to slip casting (drain) of ceramics. The liquid is poured into a preheated hollow metal mold, which has the shape of the outside of the object to be made (Figure 2.43b). The plastisol in immediate contact with the walls of the hot mold solidifies. The thickness of the cast is governed by the time of stay in the mold. After the desired time of casting is finished, the excess liquid is poured out and the solidified plastisol with the mold is kept in an oven at 350°F–400°F (176°C–204°C). The mold is then opened to remove the plastic part, which now bears on its outer side the pattern of the inner side of the

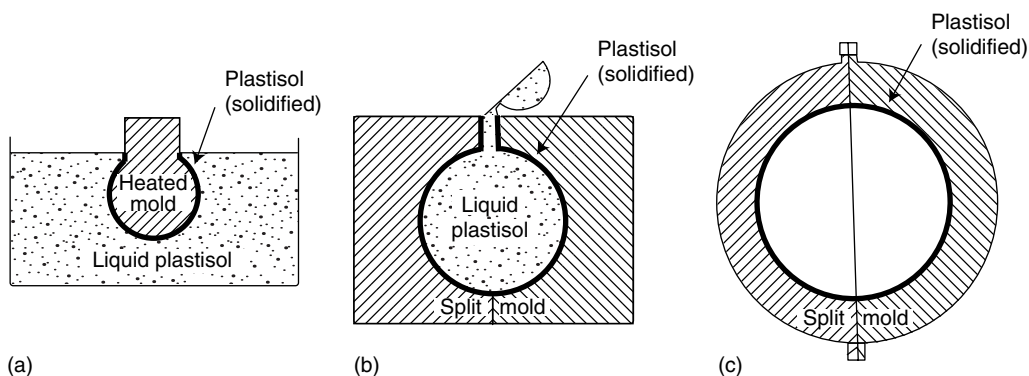


FIGURE 2.43 Plastisol casting processes: (a) dip casting; (b) slush casting; (c) rotational casting.

metal mold. Slush molding is used for hollow, open articles. Squeezable dolls or parts of dolls and boot socks are molded this way.

2.12.2.3 Rotational Casting

In rotational casting a predetermined amount of liquid plastisol is placed in a heated, closed, two-piece mold. The liquid is uniformly distributed against the walls of the mold in a thin uniform layer (Figure 2.43c) by rotating the mold in two planes. The solidified plastisol in the mold is cured in an oven; the mold is then opened, and the part is removed. The method is used to make completely enclosed hollow objects. Doll parts, plastic fruits, squeeze bulbs, toilet floats, etc. can be made by rotational casting of plastisols.

2.13 Reinforcing Processes

A RP consists of a polymeric resin strengthened by the properties of a reinforcing material [25]. Reinforced plastics occupy a special place in the industry. They are at one and the same time both unique materials into themselves and part and parcel of virtually every other segment of the plastics industry.

Reinforced plastics are composites in which a resin is combined with a reinforcing agent to improve one or more properties of the resin matrix. The resin may be either thermosetting or thermoplastic. Typical thermosetting resins used in RPs include unsaturated polyester, epoxy, phenolic, melamine, silicone, alkyd, and diallyl phthalate. In the field of reinforced thermoplastics (RTPs), virtually every type of thermoplastic material can be, and has been, reinforced and commercially molded. The more popular grades include nylon, polystyrene, polycarbonate, polypropylene, polyethylene, acetal, PVC, ABS, styrene-acrylonitrile, polysulfone, polyphenylene sulfide, and thermoplastic polyesters.

The reinforcement used in RP is a strong inert material bound into the plastic to improve its strength, stiffness, or impact resistance. The reinforcing agent can be fibrous, powdered, spherical, crystalline, or whisker, and made of organic, metallic, or ceramic material. Fibrous reinforcements are usually glass, although asbestos, sisal, cotton and high-performance fibers (discussed later) are also used. To be structurally effective, there must be a strong adhesive bond between the resin and the reinforcement. Most reinforcements are thus treated with sizes or finishes to provide maximum adhesion by the resins.

Although by definition, all RPs are composites (i.e., combinations of two materials—resin and reinforcement—that act synergistically to form a new third material RP with different properties than the original components) the term *advanced composites*, or *high-strength composites*, has taken on a special meaning. The term is applied to stiffer, higher modulus combinations involving exotic reinforcements such as graphite, boron, or other high-modulus fibers like aromatic polyamide fibers (Nomex and Kevlar) and extended-chain polyethylene fibers (Spectra ECPE). And resins like epoxy or some of the newer high heat-resistant plastics—polyamides, polyamideimide, polyquinoxalines, and polyphenylquinoxalines. Prime outlets for these materials are in the aerospace and aircraft industries.

2.13.1 Molding Methods

As mentioned above, either thermosetting and thermoplastic resin can be used as the matrix component in RPs. Today, the RTP have become an accepted part of the RPs business, although smaller than the reinforced thermosets. RTP are generally made available to the processor in the form of injection molding pellets (into which glass has been compounded) or concentrates (also a pellet but containing a much higher percentage of reinforcement, and designed to be mixed with nonreinforced pellets). It is also possible for the processor to do his own compounding of chopped glass and thermoplastic powder in injection molding.

In rotational molding and casting techniques, the processor usually adds his own reinforcement. For thermoforming, glass-RTP laminates are sold commercially. Structural foam molding of glass-RTPs and reinforcing molded urethane foams appeared as later developments in the field of RTPs.

Among thermosetting resins, unsaturated polyesters are by far the most widely used in RPs, largely because of their generally good properties, relatively easy handling, and relatively low cost. For special uses, however, other types are significant: epoxies for higher strength, phenolics for greater heat resistance, and silicones for their electrical properties and heat resistance. All these resins must be used in conjunction with a system of catalysts or curing agents in molding thermoset composites. The type and amount strongly affect the properties, working life, and molding characteristics of the resin. The polyester and epoxies are most often mixed with a catalyst just prior to molding. The most widely used catalyst for polyesters is benzoyl peroxide. Where heat is not available for curing, special catalyst-promoter systems can be used. With epoxies, an amine curing agent that reacts with the resin is most often used. However, there are many other types to choose from (see [Chapter 4](#)).

The polyester, epoxy, and thermosetting acrylic resins are usually thick liquids that become hard when cured. For this reason, they are most often combined with the reinforcement, by the molder, by dipping or pouring. There are available, however, preimpregnated reinforcements (prepregs) for the molder who wants to keep the operations as simple as possible.

Several methods are employed to make RPs. Although each method has the characteristics of either molding or casting, the process may be described as (1) hand lay-up, (2) spray-up, (3) matched molding, (4) vacuum-bag molding, (5) pressure-bag molding, (6) continuous pultrusions, (7) filament winding, and (8) prepreg molding.

2.13.1.1 Hand Lay-Up or Contact Molding

A mold is first treated with a release agent (such as wax or silicone-mold release), and a coating of the liquid resin (usually polyester or epoxy) is brushed, rolled, or sprayed on the surface of the mold. Fiberglass cloth or mat is impregnated with resin and placed over the mold. Air bubbles are removed, and the mat or cloth is worked into intimate contact with the mold surface by squeegees, by rollers, or by hand (Figure 2.44a). Additional layers of glass cloth or mat are added, if necessary, to build up the desired thickness. The resin hardens due to curing, as a result of the catalyst or hardener that was added to the resin just prior to its use. Curing occurs at room temperature, though it may be speeded up by heat. Ideally, any trimming should be carried out before the curing is complete, because the material will still be sufficiently soft for knives or shears. After curing, special cutting wheels may be needed for trimming.

Lowest-cost molds such as simple plaster, concrete, or wood are used in this process, since pressures are low and little strength is required. However, dimensional accuracy of the molded part is relatively low and, moreover, maximum strength is not developed in the process because the ratio of resin to filler is relatively high.

The hand lay-up process can be used for fabricating boat hulls, automobile bodies, swimming pools, chemical tanks, ducts, tubes, sheets, and housings, and for building, machinery, and autobody repairs.

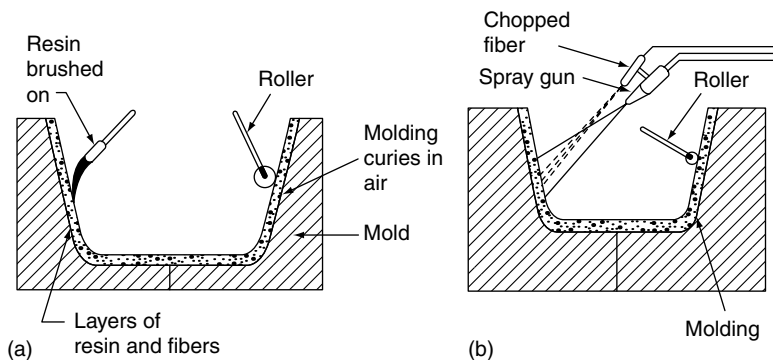


FIGURE 2.44 (a) Basic hand lay-up method. (b) Spray-up technique.

2.13.1.2 Spray-Up

A release agent is first applied on the mold surface, and measured amounts of resin, catalyst, promoter, and reinforcing material are sprayed with a multiheaded spray gun (Figure 2.44b). The spray guns used for this work are different from those used for spraying glazes, enamels, or paints. They usually consist of two or three nozzles, and each nozzle is used to spray a different material. One type, for example, sprays resin and promoter from one nozzle, resin and catalyst from another, and chopped glass fibers from a third. The spray is directed on the mold to build up a uniform layer of desired thickness on the mold surface. The resin sets rapidly only when both catalyst and promoter are present. This method is particularly suitable for large bodies, tank linings, pools, roofs, etc.

2.13.1.3 Matched Metal Molding

Matched metal molding is used when the manufacture of articles of close tolerances and a high rate of production are required. Possible methods are perform molding, sheet molding, and dough molding. In *perform molding* the reinforcing material in mat or fiber form is preformed to the approximate shape and placed on one-half of the mold, which was coated previously with a release agent. The resin is then added to the perform, the second half of the mold (also coated previously with a release agent) is placed on the first half, and the two halves of the mold are then pressed together and heated (Figure 2.45). The resin flows, impregnates the perform, and becomes hard. The cured part is removed by opening the mold. Because pressures of up to 200 psi (14 kg/cm^2) can be exerted upon the material to be molded, a higher ratio of glass to resin may be used, resulting in a stronger product. The cure time in the mold depends on the temperature, varying typically from 10 min at 175°F (80°C) to only 1 min at 300°F (150°C). The cure cycle can thus be very short, and a high production rate is possible.

The molding of sheet-molding compounds (SMC) and dough-molding compounds (DMC) is done “dry”—i.e., it is not necessary to pour on resins. SMC, also called *prepreg*, is basically a polyester resin mixture (containing catalyst and pigment) reinforced with chopped strand mat or chopped roving and formed into a pliable sheet that can be handled easily, cut to shape, and placed between the halves of the heated mold. The application of pressure then forces the sheet to take up the contours of the mold.

DMC is a doughlike mixture of chopped strands with resin, catalyst, and pigment. The charge of dough, also called premix, may be placed in the lower half of the heated mold, although it is generally wise to perform it to the approximate shape of the cavity. When the mold is closed and pressure is applied, DMC flows readily to all sections of the cavity. Curing generally takes a couple of minutes for mold temperatures from 250 to 320°F (120°C–160°C). This method is used for the production of switch gear, trays, housings, and structural and functional components.

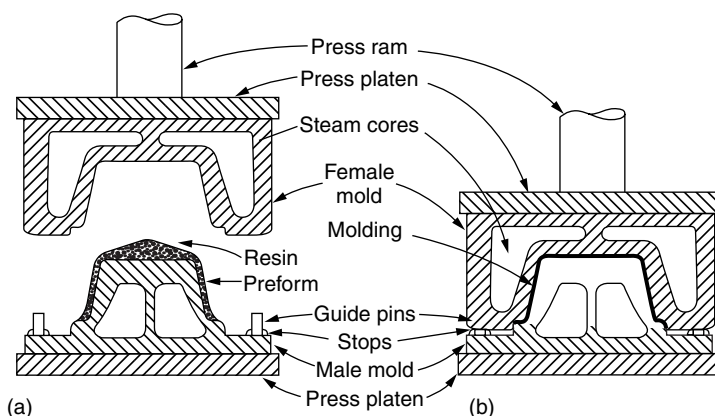


FIGURE 2.45 Matched metal molding: (a) before closing of die; (b) after closing of die.

2.13.1.4 Vacuum-Bag Molding

In vacuum-bag molding the reinforcement and the resin mixed with catalyst are placed in a mold, as in the hand layup method, and an airtight flexible bag (frequently rubber) is placed over it. As air is exhausted from the bag, atmospheric air forces the bag against the mold (Figure 2.46). The resin and reinforcement mix now takes the contours of the mold. If the bag is placed in an autoclave or pressure chamber, higher pressure can be obtained on the surface. After the resin hardens, the vacuum is destroyed, the bag opened and removed, and the molded part obtained. The technique has been used to make automobile body, aircraft component, and prototype molds.

2.13.1.5 Pressure-Bag Molding

In pressure-bag molding the reinforcement and the resin mixed with catalyst are placed in a mold, and a flexible bag is placed over the wet lay-up after a separating sheet (such as cellophane) is laid down. The bag is then inflated with an air pressure of 20–50 psi (1.4–3.5 kg/cm²). The resin and reinforcement follow the contours of the mold (Figure 2.47). After the part is hardened, the bag is deflated and the part is removed. The technique has been used to make radomes, small cases, and helmets.

2.13.1.6 Continuous Pultrusion

Continuous strands, in the form of roving or other forms of reinforcement, are impregnated with liquid resin bath and pulled through a long, heated steel die which shapes the product and controls the resin content. The final cure is effected in an oven through which the stock is drawn by a suitable pulling device. The method produces shapes with high unidirectional strength (e.g., I-beams, rods, and shafts). Polyesters account for 90% of pultrusion resin, epoxies for the balance.

2.13.1.7 Filament Winding

In the filament-winding method, continuous strands of glass fiber are used in such a way as to achieve maximum utilization of the fiber strength. In a typical process, rovings or single strands are fed from a reel through a bath of resin and wound on a suitably designed rotating mandrel. Arranging for the resin impregnated fibers to transverse the mandrel at a controlled and predetermined (programmed) manner (Figure 2.48) makes it possible to lay down the fibers in any desired fashion to give maximum strengths in the direction required. When the right number of layers have been applied, curing is done at room temperature or in an oven. For open-ended structures, such as cylinders or conical shapes, mandrel design is comparatively simple, either cored or solid steel or aluminum being ordinarily used for the purpose. For structures with integrally wound end closures, such as pressure vessels, careful consideration must be given to mandrel design and selection of mandrel material. A sand-poly(vinyl alcohol) combination, which disintegrates readily in hot water, is an excellent choice for diameters up to 5 ft (1.5 m). Thus, a mandrel made of sand with water-soluble poly(vinyl alcohol) as a binder can be

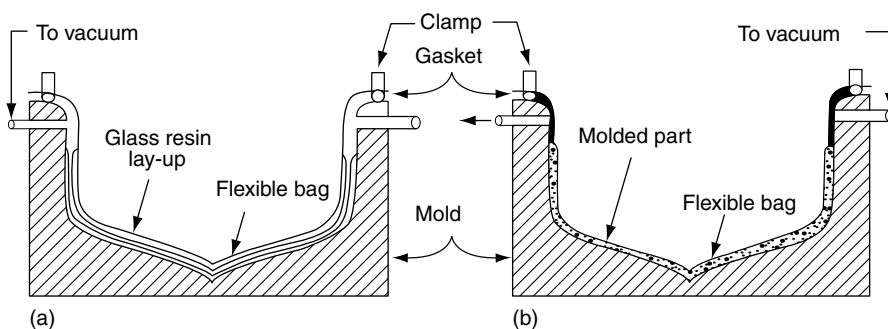


FIGURE 2.46 Vacuum-bag molding: (a) before vacuum applied; (b) after vacuum applied.

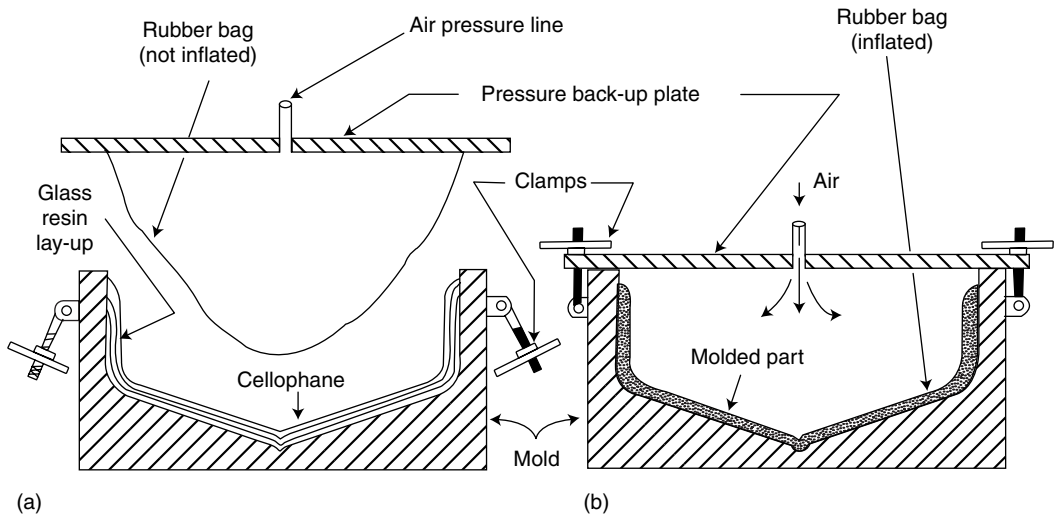


FIGURE 2.47 Pressure-bag molding: (a) during lay-up; (b) during curing.

decomposed with water to recover the filament-wound part. Other mandrel materials include low-melting alloys, eutectic salts, soluble plasters, frangible or breakout plasters, and inflatables.

Because of high glass content, filament-wound parts have the highest strength-to-weight ratio of any reinforced thermoset. The process is thus highly suited to pressure vessels where reinforcement in the highly stressed hoop direction is important. Pipe installation, storage tanks, large rocket motor cases, interstage shrouds, high-pressure gas bottles, etc., are some of the products made of filament winding. The main limitation on the process is that it can only be used for fabricating objects which have some degree of symmetry about a central axis.

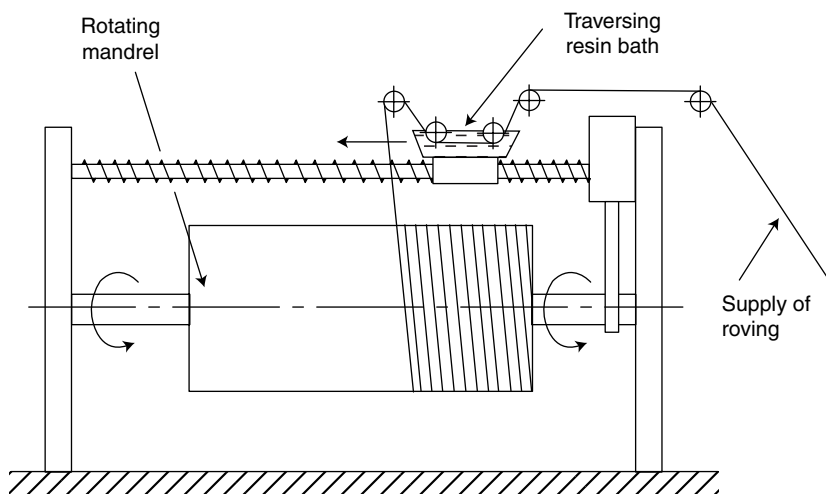


FIGURE 2.48 Sketch of filament winding.

2.13.1.8 Prepreg Molding

Optimal strength and stiffness of continuous fiber–reinforced polymeric composites is obtained through controlled orientation of the continuous fibers. One means to achieve this is by prepreg molding. In this process, unidirectionally oriented layers of fibers are pre-impregnated with the matrix resin and cured to an intermediate stage of polymerization (B-stage). When desired, this pre-impregnated composite precursor, called a prepreg, can be laid up in the required directions in a mold for quick conversion into end components through the use of hot curing techniques. Prepregs can thus be described as pre-engineered laminating materials for the manufacture of fiber–reinforced composites with controlled orientation of fibers.

For the designer, a precisely controlled ply of prepreg represents a building block, with well-defined mechanical properties from which a structure can be developed with confidence. For the fabricator, on the other hand, prepregs provide a single, easy-to-handle component that can be applied immediately to the lay-up of the part to be manufactured, be it aircraft wing skin or fishing rod tube. The prepreg has the desired handleability already built in to suit the lay-up and curing process being utilized, thus improving efficiency and consistency.

Prepregs have been used since the late 1940s, but they have only achieved wide prominence and recognition since the development of the higher performance reinforcing fibers, carbon, and kevlar. The quantum leap in properties provided by these new fibers generated a strong development effort by prepreg manufacturers and there is no doubt that new developments made in this area have been as significant, if not as evident, as that of the introduction of the new fibers.

The use of prepreg in the manufacture of a composite components offers several advantages over the conventional wet lay-up formulations:

1. Being a readily formulated material, prepreg minimizes the material's knowledge required by a component manufacturer. The cumbersome process of stocking various resins, hardeners, and reinforcements is avoided.
2. With prepreg a good degree of alignment in the required directions with the correct amount of resin is easily achieved.
3. Prepreg offers a greater design freedom due to simplicity of cutting irregular shapes.
4. Material wastage is virtually eliminated as offcuts of prepregs can be used as random molding compounds.
5. Automated mass-production techniques can be used for prepreg molding, and the quality of molded product is reproducible.
6. Toxic chemical effects on personnel using prepregs are minimized or eliminated.

A flowchart showing the key stages in the fabrication of composite structures from raw materials with an intermediate prepregging step is given in [Figure 2.49](#). It can be seen that there are two basic constituents to prepreg—the reinforcing fiber and the resin system. All of the advanced reinforcing fibers are available in continuous form, generally with a fixed filament diameter. The number of filaments that the supplier arranges into a “bundle” (or yarn) varies widely, and is an important determinant of the ability to weave fabric and make prepregs to a given thickness. In the majority of cases, the yarn is treated with a size to protect it from abrasion during the weaving or prepregging process. Often, the size is chosen such that it is compatible with the intended resin system.

Resin systems have developed into extremely complex multi-ingredient formulations in an effort to ensure the maximum property benefit from the fiber. Normally there are four methods of impregnation: (1) solution dip; (2) solution spray; (3) direct hot-melt coat; and (4) film calendaring.

The solution dip and solution spray impregnation techniques work with a matrix resin dissolved in a volatile carrier. The low viscosity of the resin solution allows good penetration of the reinforcing fiber bundles with resin. In solution dipping, the fiber, in yarn or fabric form, is passed through the resin solution and picks up an amount of solids dependent upon the speed of through-put and the solids level. With solution spraying, on the other hand, the required amount of resin formulation is metered directly

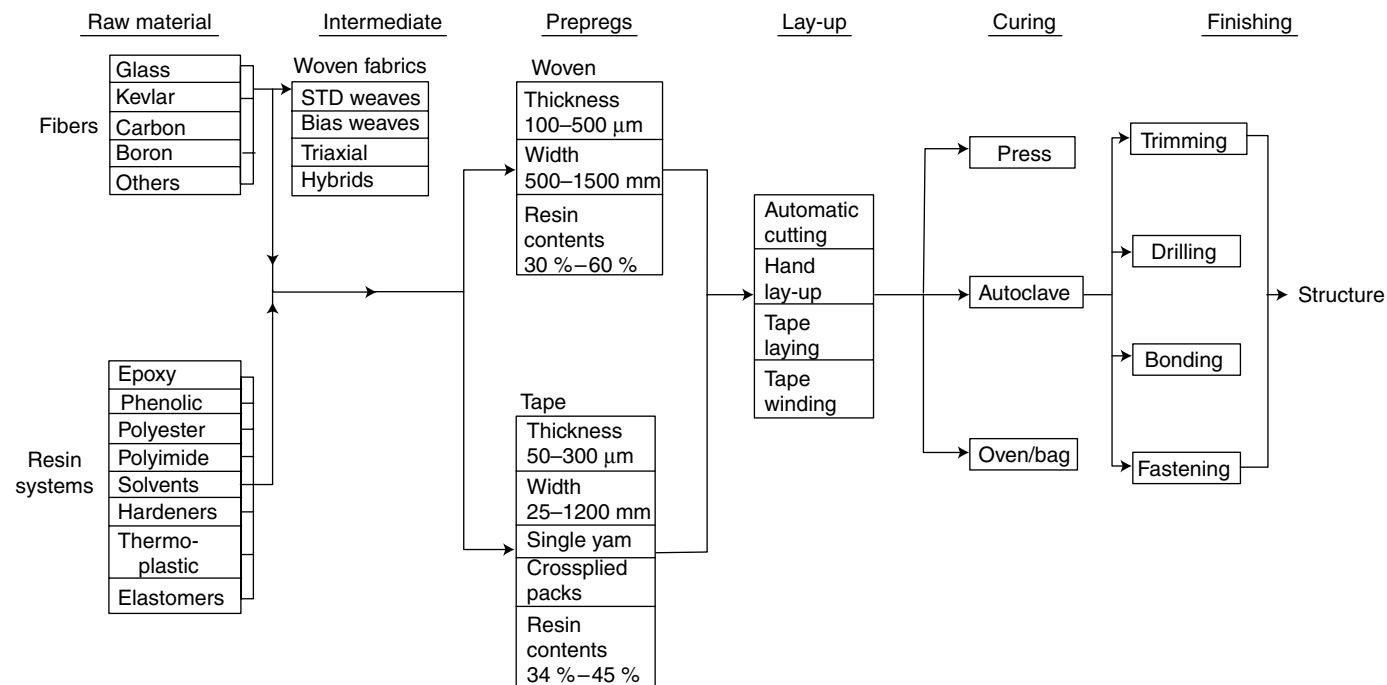


FIGURE 2.49 Flow chart showing key stages in the fabrication of composite structures from raw materials by prepreg molding. (After Lee, W. J., Seferis, J. C., and Bonner, D. C. 1986. *SAMPE Q.*, 17, 2, 58.)

onto the fiber. In both cases, the impregnated fiber is then put through a heat cycle to remove the solvent and “advance” the chemical reaction in the resin to give the correct degree of tack.

Direct hot melt can be performed in a variety of ways. In one method, the reinforcing fiber web is dipped into a melt resin bath. A doctor blade, scraper bar, or metering roller controls the resin content. Alternately, the melt resin is first applied to a release paper, the thickness of the resin being determined by a doctor blade. The melt resin on the release paper is then brought into contact with a collimated fiber bundle and pressed into it in a heated impregnation zone.

In film calendaring, which is a variation of the above method, the resin formulation is cast into a film from either hot-melt or solution and then stored. Thereafter in a separate process, the reinforcing fiber is sandwiched between two films and calendered so that the film is worked into the fiber.

The decision of which method to use is dependent upon several factors. Hot melt film processes are faster and cheaper, but certain resin formulations cannot be handled in this way, and hence solution methods have to be used. The solution dip method is often preferred for fabrics as the need to squeeze hot-melt and film into the interstices of the fabric can cause distortion of the weave pattern.

In a process based on a biconstituent tow impregnation concept, the polymeric matrix is introduced in fibrous form and a comingled tow of polymer and reinforcing fibers are fed into a heated impregnation zone (Figure 2.50). In this method, it may be possible to effect better wetout of the reinforcing fibers with the matrix polymer, especially with high viscosity thermoplastic matrix polymers, through intimate comingling.

The machines necessary to accomplish the above prepregging procedures are many and varied. There are three distinct aspects to quality control: raw material screening, on-line control, and batch testing. All three are obviously important, but the first two are more critical.

Fibers and base resins are supplied against certificates of conformance and often property test certificates. On-line control during the manufacture of prepreg revolves around the correct ratio of fiber to resin. This is done by a traversing Beta-gauge, which scans the dry fiber (either unidirectional or fabric) and then the impregnated fiber and provides a continuous real-time plot of the ratio across the width of the material. This can be linked back to the resin system application point for continuous adjustment.

Batch testing is carried out to verify prepreg properties, such as resin content, volatile level, and flow. The resin “advancement” (chemical reaction) is monitored via a Differential Scanning Calorimeter (DSC) and the formulation consistency by testing the T_g via DSC or Dynamic Mechanical Analyzer (DMA). The laminate properties are also determined. All are documented and quoted on a Release Certificate.

Commercial prepreps are available with different trade names. Fibredux 914 of Ciba-Geigy is a modified epoxy resin preimpregnated into unidirectional fibers of carbon (HM or HT), glass (E type and R type), or aramid (Kevlar 49) producing prepreps that, when cured to form fiber reinforced composite components, exhibit very high strength retention between -60°C and $+180^{\circ}\text{C}$ operational temperatures.

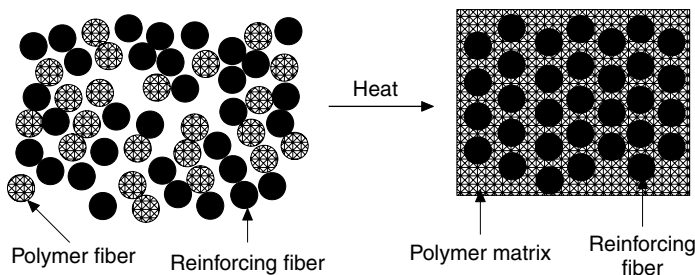


FIGURE 2.50 Biconstituent tow impregnation using a comingled tow of polymer and reinforcing fibers. (After Lee, W. J., Seferis, J. C., and Bonner, D. C. 1986. *SAMPE Q.*, 17(2), 58.)

“Scotchply” brand RPs of Industrial Specialties Division of 3M Company are structural-grade thermosetting molding materials, consisting of unidirectional nonwoven glass fibers embedded in an epoxy resin matrix. The product is available both in prepreg form in widths up to 48 in. (1.22 m) and in flat sheet stock in sizes up to 48 in. (1.22 m) \times 72 in. (1.83 m). The cured product is claimed to possess extraordinary fatigue life, no notch sensitivity, high ultimate strength, and superior corrosion resistance. The range of application of the RP includes vibratory springs, sonar housings, landing gear, picker blades, snowmobile track reinforcement, helicopter blades, seaplane pontoons, missile casing, and archery bow laminate.

2.13.2 Fibrous Reinforcements

Although many types of reinforcements are used with plastics, glass fibers predominate. Fibrous glass reinforcements are available in many forms (described below). Asbestos is used in the form of loose fiber, paper, yarn, felt, and cloth. The two largest uses of asbestos in plastics are with PVC in vinyl asbestos tile and with polyesters and polypropylene.

Most natural and synthetic fibers do not have the strength required for a RPs part. However, when intermediate strengths are satisfactory, they can be used. In this category are nylon, rayon, cotton fabrics, and paper. Sisal fibers have also found use as a low cost reinforcing material in premix molding compounds.

High-modulus graphite and carbon fibers, aramid fibers and ECPE fibers are playing a more and more important role in RPs. Boron filaments, with outstanding tensile strengths, are usually used in the form of prepreg tapes and have been primarily evaluated for the aerospace and aircraft industry.

2.13.2.1 Glass Fibers

A high-alkali “A-glass” and a low-alkali “E-glass” are used as reinforcements for polymer composites, the latter being used most often. Since the modulus of E-glass is 10.5×10^6 psi and the tensile strength upwards of 250,000 psi, it is not surprising that the stiffness and strength of most plastics can be increased by compounding with glass. A more chemical resistant glass, sodium borosilicate (C-glass), and a higher-tensile-strength glass, S-glass, are also available. E-glass is a calcium aluminosilicate, and S-glass is a magnesium aluminosilicate. Fiberglass is available as a collection of parallel filaments (roving), chopped strands, mat, and woven fabric.

Glass filaments are produced by melting a mixture of silica, limestone, and other reactants, depending on the type of glass and forcing the molten product through small holes (bushings). The hot filaments are gathered together and cooled by a water spray. These multiple glass filaments are gathered together into a bundle, called a strand, which is wound up on a coil. Short fibers (staple) are produced by passing a stream of air across the filaments as they emerge from the bushings.

Rovings are rope-like bundles of continuous untwisted strands for use in such processes as perform press molding, filament winding, spray-up, pultrusion, and centrifugal casting. They can also be converted into chopped strand mats or cut into short fibers for molding compounds.

Chopped strands of glass 1/32–1/2 in. in length can be incorporated in thermoset or thermoplastic materials about as easily as the particulate fillers. Each strand may be made up of 204 individual filament whose diameter is $2\text{--}7.5 \times 10^{-4}$ in.

Chopped strands several inches long can be loosely bound as a mat that is porous and in which the strands are randomly oriented in two dimensions. This form is suitable for impregnation by a liquid polymer. After polymerization or cross-linking (curing) under pressure, the composite will comprise a polymer-network matrix in which the individual strands are embedded.

Chopped strand mats provide nondirectional reinforcement (i.e., strengths in many directions, as contrasted to unidirectional forms which are continuous fibers, like roving, that provide strength in one direction). These mats are available in a variety of thicknesses, usually expressed in weight per square foot. In order to hold the fibers together, a resin binder is generally used, the type depending on the resin and molding process. In some cases, the mats are stitched or needled, instead of using the resin binder.

A woven glass fabric (cloth) might be used in place of the mat or in combination with it. In this case there will be a variation in strength with the angle between the axis of the fibers and the direction of stress. Twisted yarns are generally woven into fabrics of varying thickness and with tight or loose weaves, depending upon the application. Most are balanced weaves (i.e., equal amounts of yarn in each direction), although some are unidirectional (more fibers running in one direction). Although costlier, they offer a high degree of strength. Rovings can also be woven into a fabric that is less costly than the woven yarn fabrics, coarser, heavier, and easier to drape.

For optimum adhesion at the interface between the fiber surface (stationary phase) and the resin matrix (continuous phase), the glass fibers must be treated with coupling agents to improve the interfacial adhesion. The pioneer coupling agent (linking agent) was methacrylatochromic chloride (Volan). This has been supplanted by organosilanes, organotitanates, and organozirconates. These coupling agents contain functional groups, one of which is attracted to the fiber surface and the other to the resin (Figure 2.51).

2.13.2.2 Graphite Carbon Fibers

Graphite carbon fibers are the predominant high-strength, high-modulus reinforcing agent used in the fabrication of high-performance polymer composites. In general, the term *graphite fiber* refers to fibers that have been treated above 1,700°C (3,092°F) and have tensile moduli of elasticity of 5×10^5 psi (3,450 MPa) or greater. Carbon fibers are those products that have been processed below 1,700°C (3,092°F) and consequently exhibit elastic moduli up to 5×10^5 psi (3,450 MPa) [25]. A further distinction is that the carbon content of carbon fibers is 80%–95%; and that of graphite, above 99%. However, the industry has universally adopted the term “graphite.” It will therefore be used to describe both product forms in this section.

Graphite fibers were first utilized by Thomas Edison in 1880 for his incandescent lamps. The filaments were generated by the carbonization of bamboo in the absence of air. When tungsten filaments replaced the graphite in lamps, interest in graphite materials waned until the mid 1950s when rayon-based graphite fibers were created. These products exhibited relatively high tensile strengths of about 4×10^5 psi (2,760 MPa) and were designed for rocket/missile ablative component applications.

A significant event that led to the development of today's graphite industry was the utilization of PAN as a graphite precursor material by Tsunoda in 1960 [27]. Subsequent work led to continued improvement of PAN-based graphite fiber properties by numerous researchers. These development focused on stretching the PAN precursor to obtain a high degree of molecular orientation of the polymer molecules followed by stabilizing it under tensile load, carbonization, and graphitization. PAN-based graphite fibers are now available with tensile moduli of up to 1.2×10^6 psi (8,280 MPa) and tensile strengths above 8×10^5 psi (5,516 MPa).

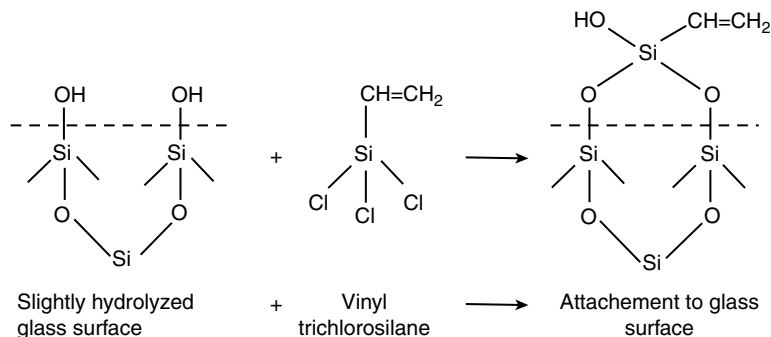


FIGURE 2.51 Mechanism of functioning of a glass surface finish.

Pitch was first identified as a graphite precursor by Otani in 1965 [28]. These fibers are made by melt spinning a low-cost isotropic molten (petroleum) pitch and then oxidizing the filaments as they are spun. This step is followed by carbonization at 1,000°C (1832°F) in an inert atmosphere. Process modifications to improve the fiber properties evolved through the 1970s until pitch-based (including mesophase liquid crystal pitch) graphite fibers with tensile strengths up to 3.75×10^5 psi (2,590 MPa) and tensile moduli to 1.2×10^6 psi (8,300 MPa) were achievable.

2.13.2.3 Fiber Manufacture

The pyrolysis of organic fibers used as graphite precursors is a multistage process. The three principal graphite precursors are PAN, pitch, and rayon, with PAN as the predominant product.

The commercial production of PAN precursor fiber is based on either dry or wet spinning technology. In both instances, the polymer is dissolved in either an organic or inorganic solvent at a concentration of 5–10% by weight. The fiber is formed by extruding the polymer solution through spinneret holes into hot gas environment (dry spinning) or into a coagulating solvent (wet spinning). The wet spinning is more popular as it produces fibers with round cross-section, whereas the dry spinning results in fiber with a dog bone cross-section.

The wet-spun precursor making process [29] includes three basic steps: polymerization, spinning, and after treatments (Figure 2.52). Acrylonitrile monomer and other comonomers (methyl acrylate or vinyl acetate) are polymerized to form a PAN copolymer. The reactor effluent solution, called “dope,” is purified, the unreacted monomers removed, and the solid contaminants filtered off. The spinning process next extrudes the purified dope through holes in spinnerettes into a coagulating solution. The spun gel fiber then passes through a series of after-treatments such as stretching, oiling, and drying. The product is the PAN precursor.

In order to produce high-strength, high-modulus graphite fibers from the PAN precursor, it is essential to produce preferred molecular orientation parallel to the fiber axis and then “stabilize” the fiber against relaxation phenomena and chain scission reactions that may occur in subsequent carbonization steps. A typical step-by-step PAN-based graphite manufacturing process begins with the aforementioned precursor stabilization which is followed by carbonization, graphitization, surface treatment, and sizing, as shown schematically in Figure 2.53.

The stabilization of the PAN precursor involves “preoxidation” by heating the fiber in an air oven at 200°C–300°C (392°F–572°F) for approximately one hour while controlling the shrinkage/tension of the fiber so that the PAN polymer is converted into a thermally infusible aromatic ladder-like structure.

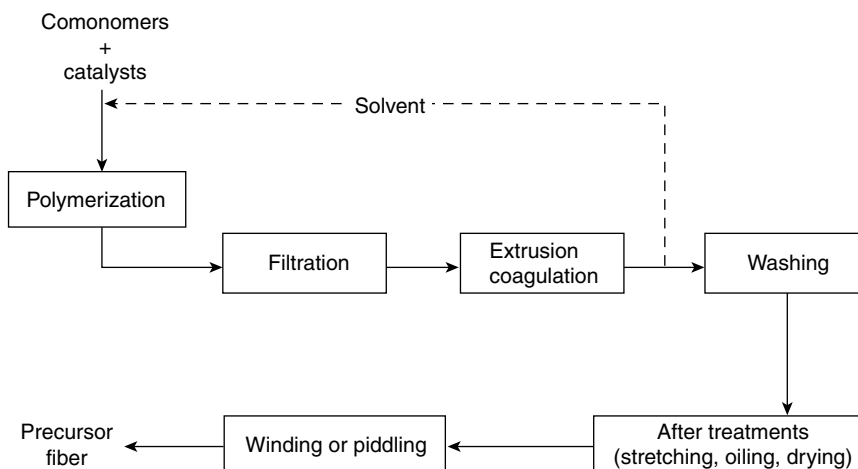


FIGURE 2.52 Typical PAN precursor manufacturing steps based on solution polymerization and wet spinning.

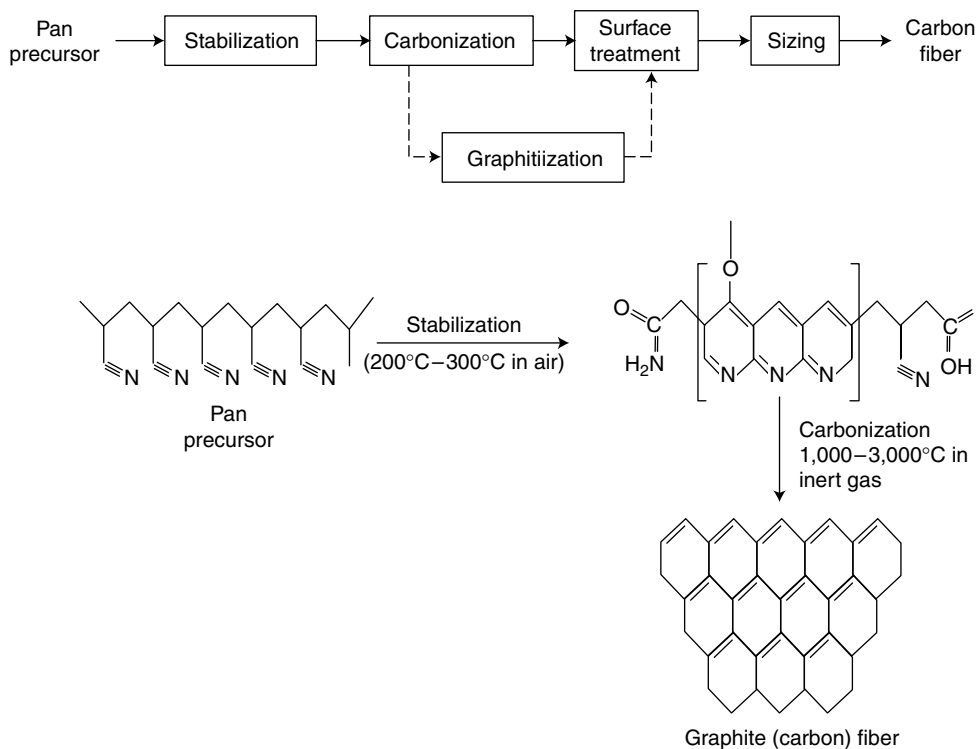


FIGURE 2.53 Schematic of a typical step-by-step PAN-based graphite manufacturing process.

The next step is the process of carbonization, which pyrolyzes the stabilized PAN-based fibers until they are transformed into graphite (carbon) fibers. The carbonization treatment is done in an inert atmosphere (generally nitrogen) at temperatures greater than 1,200°C (2,192°F). This step removes hydrogen, oxygen, and nitrogen atoms from the ladderlike polymers whose aromatic rings then collapse into a graphitelike polycrystalline structure. It is during this stage that high-mechanical-property characteristics of graphite fibers are developed. The development of these properties is directly related to the formation and orientation of graphitelike fibers or ribbons within each individual fiber.

Graphitization performed at temperatures above 1,800°C (3,272°F) is an optional treatment. Its purpose is to improve the tensile modulus of elasticity of the fiber by improving the crystalline structure and orientation of graphitelike crystallites within each individual fiber. The higher heat-treatment temperature used in graphitization also results in a higher carbon content of that fiber. The final step in the process of producing graphite or carbon fiber is surface treatment and sizing prior to bobbin winding the continuous filaments. The surface treatment is essentially an oxidation of the fiber surface to promote wettability and adhesion with the matrix resin in the composite. Sizing improves handleability and wettability of the fiber with the matrix resin. Typical sizing agents are poly(vinyl alcohol), epoxy, and polyimide.

Pitch-based graphite fibers are produced by two processes. The precursor of one of these processes is a low-softening-point isotropic pitch and the process scheme includes the following steps: (1) melt-spin isotropic pitch; (2) thermoset at relatively low temperatures for long periods of time; (3) carbonize in an inert atmosphere at 1,000°C (1,832°F); (4) stress graphitize at high temperatures 3,000°C (5,432°F). The high-performance fibers produced in this manner are relatively expensive because of the very long thermosetting time required and the need for high-temperature stress graphitization.

The commercially more significant process for making pitch-based fibers is the mesophase process, which involves the following steps: (1) heat treat in an inert atmosphere at 400–450°C (752–842°F) for an

extended period of time in order to transform pitch into a liquid-crystalline (mesophase) state; (2) spin the mesophase pitch into fibers; (3) thermoset the fibers at 300°C (572°F) for 2½ h; (4) carbonize the fibers at 1,000°C (1,832°F); and (5) graphitize the fibers at 3,000°C (5,432°F). Since long thermosetting times and stress graphitization treatment are not required, the high-temperature graphite fibers produced by this process are lower in cost.

The process by which rayon precursor is converted to graphite fibers includes four steps: (1) fiber spinning; (2) stabilization at 400°C (752°F) for long periods of time; (3) carbonization at 1,300°C (2,372°F); and (4) stress graphitization at high temperatures 3,000°C (5,432°F). The rayon-based graphite fibers produced in this manner tend to be relatively expensive because of the very long stabilization times required and the need for stress graphitization at high temperatures.

2.13.2.4 Properties and Applications

The excellent properties of graphite are directly attributable to the highly anisotropic nature of the graphite crystal. The standard-grade PAN-based graphite fibers, which make up the largest part of both the commercial and aerospace markets have tensile strengths ranging from 4.5×10^5 to 5.5×10^5 psi (3,100–3,800 MPa) and moduli of approximately 340,000 psi (2,345 MPa). A family of intermediate-modulus/high-strain fibers with tensile strengths up to 7×10^5 psi (4,800 MPa) and modulus above 4×10^5 psi (2,760 MPa) have been developed to meet high-performance aerospace requirements. The high-modulus fibers (both PAN- and pitch-based), used in high stiffness/low-strength applications, such as space hardware, have tension moduli ranging from 5×10^5 to 1.2×10^6 psi (3,450–8,280 MPa) and strain to failures generally greater than or equal to 1%.

Graphite fibers are available to the user in a variety of forms: continuous filament for filament winding, braiding, or pultrusion; chopped fiber for injection or compression molding; impregnated woven fabrics and unidirectional tapes for lamination.

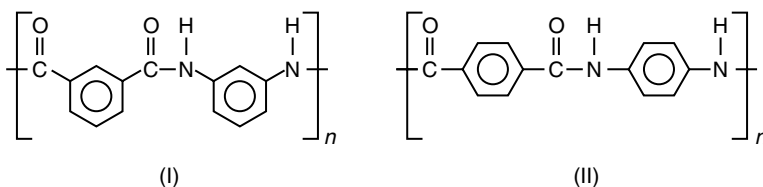
The major markets for advanced graphite fiber composites are aerospace, marine, automotive, industrial equipment, and recreation. Military aerospace applications dominate the market and military consumptions are slated to increase rapidly as programs, which utilize a very high percentage of composites move from development to large-scale production. Graphite fiber usage in space applications is in a large measure linked to Space Station programs and production activities.

Examples of nonaerospace military applications include portable, rapid deployment bridges for the army and propeller shafts for submarines. Fiber usage in the commercial aerospace sector is also growing. Commercial planes such as Boeing 767 and the Airbus A320 utilize two to three times the graphite fiber per plane that is used in older commercial models.

The biggest industrial market potential of graphite fibers is in the automotive sector. The graphite composite usage in this area should increase as lower-cost fibers become available. A major and growing use of chopped graphite fibers in the industrial market is as a reinforcement for thermoplastic-injection-molding compounds. The advantages of such use include greater strength and stiffness, higher creep and fatigue resistance, increased resistance to wear, higher electrical conductivity, and improved thermal stability and conductivity.

2.13.2.5 Aramid Fibers

Aramid fiber is the generic name for aromatic polyamide fibers. As defined by the U.S. Federal Trade Commission, an aramid fiber is a “manufactured fiber in which the fiber forming substance is a long chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings”:



Among the commercially available aramid fibers are Du Pont's Nomex (I) and Kevlar (II); in fact these trade names are commonly used in lieu of the generic name. Kevlar 49 is a high-modulus aramid fiber and is the most widely used reinforcing aramid fiber. Kevlar 29 has a lower modulus and Kevlar 149 has a higher modulus than Kevlar 49. Aromatic polyamides are described in greater detail in [Chapter 4](#).

Aramid fibers can be used to advantage to obtain composites having lighter weight, greater stiffness, higher tensile strength, higher impact resistance, and lower notch sensitivity than composites incorporating E-glass or S-glass reinforcement. Weight savings over glass result from the lower specific gravity of aramid fibers, 90.4 lb/in.³ (1.45 g/cm³) versus E-glass, 159.0 lb/in.³ (2.55 g/cm³). Higher stiffnesses are reflected in a Young's modulus up to 19×10^6 psi (1.31×10^5 MPa) for Kevlar 49 and 27×10^6 psi (1.86×10^5 MPa) for Kevlar 149, compared to 10^7 psi (6.9×10^4 MPa) for E-glass and 12×10^6 psi (8.6×10^4 MPa) for S-glass. Aramid composites are more insulating than their glass counterparts, both electrically and thermally, more damped to mechanical and sonic vibrations, and are transparent to radar and sonar. Despite their outstanding mechanical properties, these high-modulus organic fibers have the processability normally associated with conventional textiles. This leads to wide versatility in the form of the reinforcement, e.g., yarns, rovings, woven and knit goods, felts, and papers.

2.13.2.6 Applications

Fabrics woven from Kevlar 49 aramid fiber are often used as composite reinforcement, since fabrics offer biaxial strength and stiffness in a single ply. The mechanical properties of Kevlar 49 aramid are dependent on the fabric construction. The composite properties are functions of the fabric weave and the fiber volume fraction (typically 50%–55% with ply thickness 5–10 mils, depending on fabric construction). In 1987, Du Pont introduced high-modulus Kevlar 149. Compared to Kevlar 49 it has higher performance (47% modulus increase) and lower dielectric properties (65% decrease in moisture regain).

Over the past three decades, Kevlar has gained wide acceptance as a fiber reinforcement for composites in many end uses, such as tennis rackets, golf clubs, shafts, skis, ship masts, and fishing rods. The boating and aircraft industries make extensive use of advanced composites. The advanced composites have allowed innovative designers to move ahead in designing aircraft with unprecedented performance.

The cost of high-modulus aramid fibers is higher than E-glass and equivalent to some grades of S-glass on a unit-weight basis. Price differences versus glass are, however, reduced by about half on a unit volume basis when lower density of the aramids is taken into account.

For many applications, fabrics containing more than one fiber type offer significant advantages. Hybrids of carbon and Kevlar 49 aramid yield greater impact resistance over all-carbon construction and higher compressive strength over all-Kevlar construction. Hybrids of Kevlar 49 and glass offer enhanced properties and lower weight than constructions containing glass as the sole reinforcement and are less expensive than constructions using only Kevlar 49 reinforcement.

2.13.2.7 Extended-Chain Polyethylene Fibers

Extended-Chain Polyethylene Fibers (ECPE) fibers are relatively recent entrants into the high-performance fibers field. Spectra ECPE, the first commercially available ECPE fiber and the first in

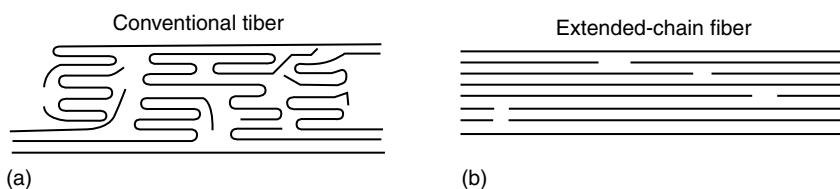


FIGURE 2.54 Fiber morphology of polyethylene. (a) Conventional PE fiber characterized by relatively low molecular weight, moderate orientation, and crystalline regions chain folded. (b) Extended-chain PE fiber characterized by very high molecular weight, very high degree of orientation, and minimum chain folding.

family of extended chain polymers manufactured by Allied-Signal, Inc. was introduced in 1985. ECPE fibers are arguably the highest modulus and highest strength fibers made. These are being utilized as a reinforcement in such applications as ballistic armor, impact shields, and radomes to take advantage of the fiber's unique properties.

Polyethylene is a flexible molecule that normally crystallizes by folding back on itself (see [Chapter 1](#)). Thus fibers made by conventional melt spinning do not possess outstanding physical properties. ECPE fibers, on the other hand, are made by a process that results in most of the molecules being fully extended and oriented in the fiber direction, producing a dramatic increase in physical properties. Using a simple analogy, the structure of ECPE fibers can be described as that of a bundle of rods, with occasional entangled points that tie the structure together. Conventional PE, by comparison, is comprised of a number of short-length chain folds that do not contribute to material strength (see [Figure 2.54](#)). ECPE fibers are, moreover, made from ultrahigh molecular weight polyethylene (UHMWPE) with molecular weight generally 1–5 million that also contributes to superior mechanical properties. Conventional PE fibers, in comparison, have molecular weights in the range 50,000 to several hundred thousand. ECPE fibers exhibit a very high degree of crystalline orientation (95%–99%) and crystalline content (60%–85%).

High-modulus PE fibers can be produced by melt extrusion and solution spinning. The melt extrusion process leads to a fiber with high modulus but relatively low strength and high creep whereas solution spinning in which very high-molecular-weight PE is utilized yields a fiber with both high modulus and high strength. The solution spinning process for a generalized ECPE fiber starts with the dissolution of polyethylene of approximately 1–5 million molecular weight in a suitable solvent. This serves to disentangle the polymer chains, a key step in achieving an extended chain polymer structure. The solution must be fairly dilute to facilitate this process, but viscous enough to be spun using conventional melt spinning equipment. The cooling of the extrudate lends to the formation of a fiber that can be continuously dried to remove solvent or later extracted by an appropriate solvent. The fibers are generally postdrawn prior to final packaging.

The solution spinning process is highly flexible and can provide an almost infinite number of process and product variations of ECPE fibers. Fiber strengths of $(3.75\text{--}5.60) \times 10^5$ psi (2,890–3,860 MPa) and tensile moduli of $(15\text{--}30) \times 10^6$ psi $[(103\text{--}207) \times 10^3$ MPa] have been achieved. The properties are similar to other high-performance fibers; however, because the density of PE is approximately two-thirds that of high modulus aramid and half that of high-modulus carbon fiber, ECPE fibers possess extraordinarily high specific strengths and specific moduli. Figure 2.54 compares the specific strength versus specific modulus for currently available fibers.

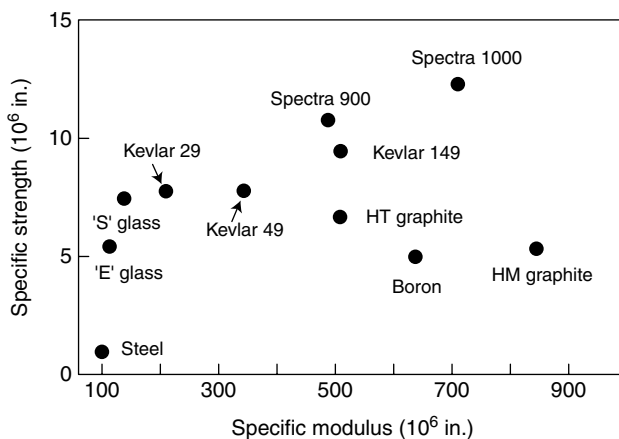


FIGURE 2.55 Comparative properties of various reinforcing fibers.

Traditional binders and wetting agents are ineffective in improving resin adhesion to polyethylene. For ECPE fibers, this characteristic is actually advantageous in specific areas. For instance, ballistic performance is inversely related to the degree of adhesion between the fiber and the resin matrix. However, for applications requiring higher levels of adhesion and wetout, it has been shown that by submitting ECPE fiber to specific surface treatments, such as corona discharge or plasma treatments, the adhesion of the fiber to various resins can be dramatically increased.

The chief application areas being explored and commercialized for ECPE fibers are divided between traditional fiber applications and high-tech composite applications. The former include sailcloth, marine ropes, cables, sewing thread, nettings, and protective clothing. The latter includes impact shields, ballistics, radomes, medical implants, sports equipment, pressure vessels, and boat hulls.

ECPE fibers (such as Spectra 1,000) are well suited for high-performance yachting sails, offering, in addition, resistance to sea water and to typical cleaning solutions used in the sailing industry, such as bleach. The major sport equipment applications to date have been canoes, kayaks, and snow and water skis. Numerous other sport applications are under development.

The high-strength, lightweight, low-moisture absorption and excellent abrasion resistance of ECPE make it a natural candidate for marine rope. In marine rope applications, load, cycling, and abrasion resistance are critical. Thus a 12-strand ECPE braid, for example, is reported to withstand about eight times the number of cycles that cause failure in 12-strand aramid braid.

Specially toughened and dimensionally stabilized ECPE yarn has been used in a revolutionary new line of cut-resistant products. ECPE fibers are being used to produce cut-resistant gloves, arm guards, and chaps in such industries as meat packing, commercial fishing, and poultry processing and in sheet metal work, glass cutting, and power tool use.

ECPE's high strength and modulus and low specific gravity offer higher ballistic protection at lower density per area than is possible with currently used materials. The significant applications include flexible and rigid armor. Flexible armor is manufactured by joining multiple layers of fabric into the desired shape, the ballistic resistance being determined by the style of the fabric and the number of layers. Traditional rigid armor can be made by utilizing woven ECPE fiber in either thermoset or thermoplastic materials. Ballistics are currently the dominant market segment. Products include helmets, helicopter seats, automotive and aircraft armor, armor radomes, and other industrial structures.

The radome (radome protective domes) market is also important for ECPE fibers. ECPE composite systems act as a shield that is virtually transparent to microwave signals, even in high-frequency regimes.

2.14 Reaction Injection Molding

A new type of injection molding called Reaction Injection Molding (RIM) has become important for fabricating thermosetting polymers [30,31]. RIM differs from the conventional injection molding in that the finished product is made directly from monomers or low-molecular-weight polymeric precursors (liquid reactants), which are rapidly mixed and injected into the mold even as the polymerization reaction is taking place. Thus, synthesis of polymer prior to molding is eliminated, and the energy requirements for handling of monomers are much less than those for viscous polymers.

For RIM to be successful, the monomers or liquid reactants must be fast reacting, and the reaction rates must be carefully synchronized with the molding process. Thus the polymers most commonly processed by RIM are polyurethanes and nylons though epoxies, and certain other polymers such as polycyclopentadiene have been processed by RIM. The process uses equipment that meters reactants to an accuracy of 1%, mixes them by high-pressure impingement, and dispenses the mixture into a closed mold. The mold is, in fact, a chemical reactor. The reaction in RIM takes place in a completely filled mold cavity. Reinforcing fillers are sometimes injected into the mold along with the reactants, a process called reinforced reaction injection molding (RRIM). In the mold the functional groups of the liquid

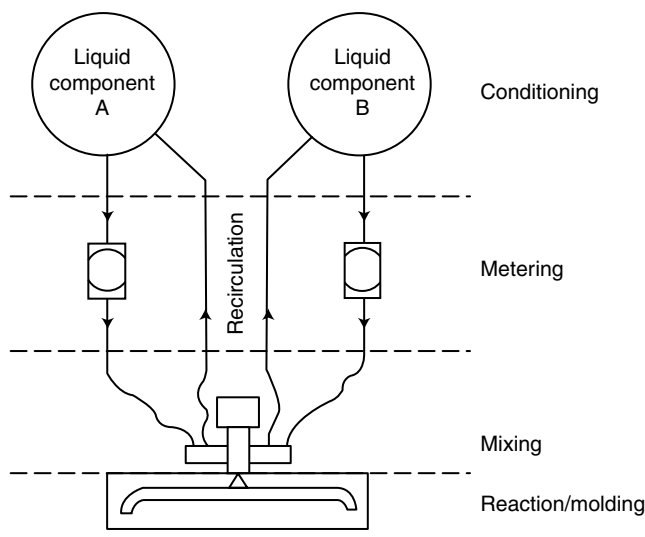


FIGURE 2.56 Schematic of RIM process.

reactants react to form chemical linkages, producing solid polymers, which comprise polymeric chains or networks depending on the starting materials. The temperature of the mold plays a vital role in the polymerization of reactants.

To produce a molded part by the RIM process requires precise but realistic process control. Figure 2.56 shows a simplified schematic of the RIM process. The important elements of the process are conditioning, metering, mixing, and molding. All the liquid reactants require precise temperature control. The flow property (viscosity) of the liquid reactants usually varies with temperature as does the density. For accurate metering the temperature must be controlled within very narrow limits. This is usually accomplished by recirculating reactants from conditioning or storage tanks designed to maintain raw material temperatures specified by the system supplier. These conditions are normally quite moderate (30°C–38°C) for polyurethanes.

For some polymerization systems, such as nylon which is processed at a high temperature, the machines are designed with heated lines and temperature control devices for pumps, mixers, and other components. The molds are also designed to control temperatures as the reaction characteristics of the RIM process are exothermic. A higher temperature increases the reaction rate, which results in an decrease of cycle time. For polyurethane, however, speeding the reaction rate by operating the mold at elevated temperatures is to be avoided, as this changes the types of linkages produced (see “Polyurethanes” in Chapter 4).

Polyurethane RIM systems have been commercial in the United States for about 50 years and a bit longer in Europe. It is still a rapidly growing field of technology. The automotive industries in the United States account for most of the commercial RIM production. A later development for RIM polyurethane, and to a lesser extent RIM nylons, is the application for housings of various instruments and appliances: computer housings, business machine housings, TV and radio cabinets, instrument cases, and similar electronic product enclosures. While elastomeric RIM is most commonly used in these applications, some housings are also molded from RIM structural foam.

Though systems suppliers do not always clearly differentiate between elastomeric and structural RIM, elastomeric RIM is molded in thin cross-section (usually 0.125 in.) at high density while structural foam has an interior foam structure, a density about one-third that of elastomeric RIM, and is molded in thicker cross-section (usually 0.375 in.).

2.14.1 Machinery

Conditioning and temperature control are accomplished by recirculating reactants from storage tanks which are jacketed and/or contain tempering coils to maintain the process temperature required by the chemical system.

RIM parts (especially polyurethanes) are usually removed from the mold before the chemical reactions that develop the physical properties are complete. The part is placed on a support jig that holds it in its final shape until it is fully cured. In some cases this is done by simply setting the supported part aside for 12–24 h. More often the supported part is postcured in an oven for several hours at temperatures of about 180°F (82°C). Nylons are completely reacted in the mold and postcuring is not necessary.

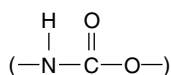
RIM polyurethanes made with aromatic isocyanates (such as pure or polymeric MDI) have a tendency to darken as a result of the effect of UV light on the chemical ring structure of the MDI component. Soft white limestone or fine carbon black is often used as filler to mask the effect of this color change.

Polyurethanes manufactured with aliphatic isocyanates are light stable, and products are molded in a wide range of bright colors. Especially interesting is the development of equipment to add color concentrate, usually dispersed in a polyol, directly into the mixing head attached to a given mold. The basic urethane formula is adjusted to compensate for the additional reactive polyol. Using this technique with a multiclamp RIM line, it is possible to mold different colors using a single RIM machine. In some cases, aromatic RIM systems are molded in color then painted the same color. This technique eliminates the need to touch up every dent or scratch which would otherwise show up tan or white.

There are several systems for painting RIM parts. Usually, RIM parts are simply primed and painted. Before painting, however, the part is cleaned to remove mold-release agents. The most common mold releases are metal stearates (or soaps) that can be removed from the part by a water wash and paraffin waxes that are usually removed by solvent vapor degreasing. Silicone mold releases are to be avoided as they are very difficult to remove from the part, and paint will not stick to the silicone surface film.

2.14.2 Polyurethanes

The most common chemicals used in the RIM process for polyurethanes are isocyanates containing two or more isocyanate (—N=C=O) groups and polyols, which contain two or more hydroxyl (—OH) groups. These reactive end-groups, so named because they occur at the ends of the chemical structure, react chemically to form a urethane linkage:



The chemical system, must be adjusted so that the number of isocyanates and hydroxyls balance and that all reactive end-groups are used in the formation of urethane linkages.

The number of polymer structures that can be formed using the urethane reaction is quite large. There are ways to produce polyurethanes having different physical properties (see “[Polyurethanes](#)” in [Chapter 4](#)). If linear polyols are reacted with diisocyanates, a flexible polyurethane will be formed. If a low boiling liquid, such as Refrigerant-11 (R-11), is incorporated into the system, the heat of reaction will produce a cellular structure. The resulting product will be flexible polyurethane foam.

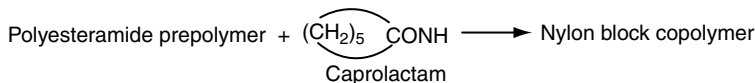
The physical properties of these materials can be varied by selecting polyols with shorter or longer polyol chains. The most common polyol or macroglycol chains are polyethers and polyesters (Chapter 4). The composition of these thermoplastic chains also plays a role in the physical properties of the end product. These chain segments in the block copolymer are often referred to as “soft” blocks, or segments, while the polyurethane segments formed by the reaction of diisocyanate with glycol are referred to as “hard” blocks or segments.

In addition to changing the chain composition and length, the physical properties can be varied by blending up to approximately 10% of a long-chain triol (such as a triol adduct of ethylene oxide and propylene oxide with glycerol) into the basic resin system formulation. This produces branching in the

“soft” segment of the block copolymer. Excessive triol modification may, however, diminish physical properties. Use of short-chain triols such as glycerol will produce cross-linking in the “hard” segments of the polymer chain. The formation of hard blocks and cross-linking in the hard block tend to produce a stiffer, more rigid product. The hard blocks tend to be crystalline and reinforce the amorphous polymer, improving its strength.

2.14.3 Nylons

RIM nylons, like polyurethanes, form polymers very rapidly by the reaction of chemical end-groups. The linkages produced are as follows:



Equipment used to manufacture RIM products must be extensively rebuilt to process RIM nylons. Because the viscosity of nylon RIM systems is low and the ingredients are quite reactive, leakage at the seals and the volumetric efficiency of the metering pumps (that is, the amount of material actually pumped divided by the volume displaced by the metering pumps) may cause problems, which require special attention. Hence, most manufacturers recommend having the machine designed specifically for nylon RIM systems.

The first commercial product made from nylon RIM was a front quarter panel (fender) for the Oldsmobile Omega Sport. Because of the excellent impact strength of nylon RIM, it has been used for bumper covers and automobile *fascia*. It also finds application in housings for business machines and electronics.

2.15 Structural Reaction Injection Molding

Structural reaction injection molding (SRIM) may be considered as a natural evolution of RIM. It is a very attractive composite manufacturing process for producing large, complex structural parts economically. The basic concepts of the SRIM process are shown in Figure 2.57. A preformed reinforcement is placed in a

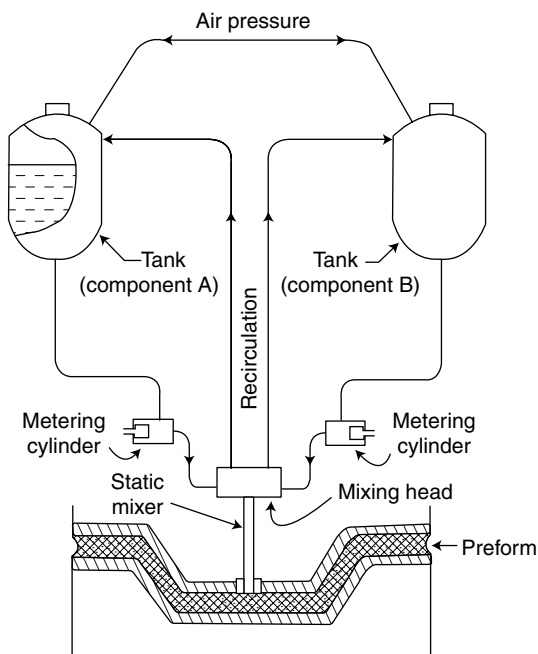


FIGURE 2.57 Schematic of structural reaction injection molding (SRIM).

closed mold, and a reactive resin mixture that is mixed by impingement under high pressure in a specially designed mix head (like that in RIM) flows at low pressure through a runner system to fill the mold cavity, impregnating the reinforcement material in the process. Once the mold cavity is filled, the resin quickly completes its reaction. A completed component can often be removed from the mold in as little as one minute.

SRIM is similar to RIM in its intensive resin mixing procedures and its reliance on fast resin reaction rates. It is also similar to resin transfer molding (RTM) (discussed later in this chapter) in employing performs that are preplaced in the cavity of a compression mold to obtain optimum composite mechanical properties. The term *structural* is added to the term *RIM* to indicate the more highly reinforced nature of the composite components manufactured by SRIM.

The key to SRIM is the perform. It is a preshaped, three-dimensional precursor of the part to be molded and does not contain the resin matrix. It can consist of fibrous reinforcements, core materials, metallic inserts, or plastic inserts. The reinforcements, cores, or inserts can be anything available that meets the economic, structural, and durability requirements of the parts. This tremendous manufacturing freedom allows a variety of alternative perform constructions.

Most commercial SRIM applications have been in general industry or in the automotive industry. The reinforcement material most commonly used has been fiberglass, due to the low cost. Fiberglass has been used in the form of woven cloth, continuous strand mat, or chopped glass.

Space-shaping cores can be used in the SRIM process to fabricate thick, three-dimensional parts with low densities. Specific grades of urethane-based foams, having densities of 6–8 lb/ft³ and dimensional stability at SRIM molding temperatures, are commonly used as molded core materials. Fiberglass reinforcements and inserts can be placed around these cores, resulting in SRIM parts, molded in one piece, that are very light-weight and structurally strong and stiff. Metallic inserts can be used in SRIM parts as local stiffeners, stressed attachment points, or weldable studs. The metallic material of choice is usually steel.

SRIM is a very labor-intensive process, and the consistency from preform to perform is usually poor. However, for very low manufacturing volumes this process can be cost-effective.

Most SRIM resins have several characteristics in common: their liquid reactants have room-temperature viscosity below 200 cps; their viscosity-cure curves are sigmoidal in shape, the typical mold-fill time being 10–90 sec; and their demold time is from 60 to 180 sec, varying with catalyst concentration. The low viscosity of SRIM resins and their relatively long fill times are crucial in allowing them to penetrate and flow through their reinforcing performs.

The design of the gating and runner configuration (if any) is usually kept proprietary by the molder. However, it appears that most SRIM parts are center-gated, with vents located along the periphery of the part. This configuration allows the displaced air in the mold cavity to be expelled uniformly.

2.15.1 Applications

The ability of SRIM to fabricate large, lightweight composite parts, consisting of all types of precisely located inserts and judiciously selected reinforcements, is an advantage that other manufacturing processes find difficult to match. Moreover, large SRIM parts can often be molded in 2–3 min, using clamping pressures as low as 100 psi. The capital requirements of SRIM are thus relatively low.

The first commercially produced SRIM part was the cover of the sparetire well in several automobiles produced by General Motors. Since then, SRIM automotive structural parts have included foamed door panels, instrument panel inserts, sunshades, and rear window decks. Nonautomotive applications include satellite dishes and seat shells for the furniture market.

2.16 Resin Transfer Molding

RTM is similar to SRIM. In its common form, RTM is a closed-mold, low-pressure process in which dry, preshaped reinforcement material is placed in a closed mold and a polymer solution or resin is injected at

a low pressure, filling the mold and thoroughly impregnating the reinforcement to form a composite part. The mold pressure in the RTM process is lower than in both SRIM and RIM/RRIM and the molding cycle time is much longer. The reinforcement and resin may take many forms, and the low pressure combined with the preoriented reinforcement package, affords a large range of component sizes, geometries, and performance options.

RTM is an excellent process choice for making prototype components. It allows representative prototypes to be molded at low cost, unlike processes such as compression molding and injection molding, which require tools and equipment approaching actual production level.

When prototyping with RTM, less reactive resins are generally used, allowing long fill times and easier control of the vents. Sizes can range from small components to very large, complex, three-dimensional structures. RTM provides two finished surfaces and controlled thickness, while other processes used for prototyping, such as hand lay-up and wet molding, give only a single finished surface.

2.17 Foaming Processes

Plastics can be foamed in a variety of ways. The foamed plastics, also referred to as cellular or expanded plastics, have several inherent features which combine to make them economically important. Thus, a foamed plastic is a good heat insulator by virtue of the low conductivity of the gas (usually air) contained in the system, has a higher ratio of flexural modulus to density than when unfoamed, has greater load-bearing capacity per unit weight, and has considerably greater energy-storing or energy-dissipating capacity than the unfoamed material. Foamed plastics are therefore used in the making of insulation, as core materials for load-bearing structures, as packaging materials used in product protection during shipping, and as cushioning materials for furniture, bedding, and upholstery.

Among those plastics which are commercially produced in cellular form are polyurethane, PVC, polystyrene, polyethylene, polypropylene, epoxy, phenol-formaldehyde, urea-formaldehyde, ABS, cellulose acetate, styrene-acrylonitrile, silicone, and ionomers. However, note that it is possible today to produce virtually every thermoplastic and thermoset material in cellular form. In general, the basic properties of the respective polymers are present in the cellular products except, of course, those changed by conversion to the cellular form.

Foamed plastics can be classified according to the nature of cells in them into closed-cell type and open-cell type. In a closed-cell foam each individual cell, more or less spherical in shape, is completely closed in by a wall of plastic, whereas in an open-cell foam individual cells are inter-connecting, as in a sponge. Closed-cell foams are usually produced in processes where some pressure is maintained during the cell formation stage. Free expansion during cell formation typically produces open-cell foams. Most foaming processes, however, produce both kinds.

A closed-cell foam makes a better buoy or life jacket because the cells do not fill with liquid. In cushioning applications, however, it is desirable to have compression to cause air to flow from cell to cell and thereby dissipate energy, so the open-cell type is more suitable. Foamed plastics can be produced in a wide range of densities—from 0.1 lb/ft.³ (0.0016 g/cm³) to 60 lb/ft.³ (0.96 g/cm³)—and can be made flexible, semirigid, or rigid.

A rigid foam is defined as one in which the polymer matrix exists in the crystalline state or, if amorphous, is below its T_g . Following from this, a flexible cellular polymer is a system in which the matrix polymer is above its T_g . According to this classification, most polyolefins, polystyrene, phenolic, polycarbonate, polyphenylene oxide, and some polyurethane foams are rigid, whereas rubber foams, elastomeric polyurethanes, certain polyolefins, and plasticized PVC are flexible. Intermediate between these two extremes is a class of polymer foams known as semirigid. Their stress-strain behavior is, however, closer to that of flexible systems than to that exhibited by rigid cellular polymers.

The group of rigid cellular polymers can be further subdivided according to whether they are used (1) for non-load-bearing applications, such as thermal insulation; or as (2) load-bearing structural materials, which require high stiffness, strength and impact resistance.

The description of cellular foams as low, medium or high density is very common in practice. This is, however, not exact as the different density ranges which correspond to each of these items are not strictly defined. The following figures can, however, serve as a rough general guide:

	lb/ft. ³	Kg/m ³
Low density	0.1–3	2–50
Medium density	3–21	50–350
High density	21–60	350–960

(Note that the density of a polymer foam refers to its bulk density, defined by the ratio of total weight/total volume of the polymer and gaseous component. Obviously the gas phase contributes considerably to the volume of the end product, while the solid component contributes almost to the entire weight.)

Obtained forms of foamed plastics are blocks, sheets, slabs, boards, molded products, and extruded shapes. These plastics can also be sprayed onto substrates to form coatings, foamed in place between walls (i.e., poured into the empty space in liquid form and allowed to foam), or used as a core in mechanical structures. It has also become possible to process foamed plastics by conventional processing machines like extruders and injection-molding machines.

Polymer foams may be homogeneous with a uniform cellular morphology throughout or they may be structurally anisotropic. They may have an integral solid polymer skin or they may be multicomponent in which the polymer skin is of different composition to the polymeric cellular core. Schematic representations of the different physical forms of cellular polymers are given in Figure 2.58. Some

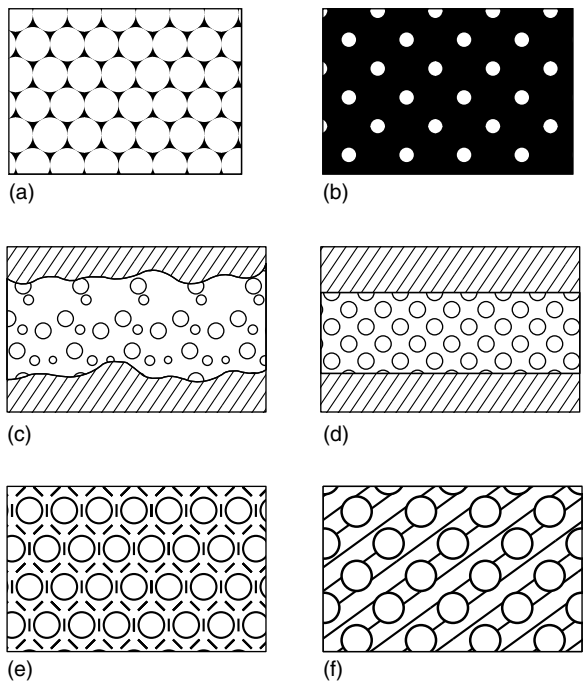


FIGURE 2.58 Schematic representations of section through different types of cellular polymer. (a) Low-density open-cell foam. (b) High-density closed-cell foam. (c) Single-component structural foam with cellular core and integral solid skin. (d) Multicomponent structural foam. (e) Fiber-reinforced closed-cell foam. (f) Syntactic foam.

special types of foams, namely, structural foams, reinforced foams, and syntactic foams are represented by Figure 2.58c to Figure 2.58f. These are described in a later section.

Foaming of plastics can be done in a variety of ways. Most of them typically involve creating gases to make foam during the foaming cycle. Once the polymer has been expanded or “blown,” the cellular structure must be stabilized rapidly; otherwise it would collapse. Two stabilization methods are used. First, if the polymer is a thermoplastic, expansion is carried out above the softening or melting point, and the form is then immediately cooled to below this temperature. This is called physical stabilization. The second method—chemical stabilization—requires the polymer to be cross-linked immediately following the expansion step. Common foaming processes are the following:

1. Air is whipped into a dispersion or solution of the plastic, which is then hardened by heat or catalytic action or both.
2. A low-boiling liquid is incorporated in the plastic mix and volatilized by heat.
3. Carbon dioxide gas is produced within the plastic mass by chemical reaction.
4. A gas, such as nitrogen, is dissolved in the plastic melt under pressure and allowed to expand by reducing the pressure as the melt is extruded.
5. A gas, such as nitrogen, is generated within the plastic mass by thermal decomposition of a chemical blowing agent.
6. Microscopically small hollow beads of resin or even glass (e.g., microballoons) are embedded in a resin matrix.

Foams can be made with both thermoplastic and thermosetting plastics. The well known commercial thermoplastic foams are polystyrene, PVC, polyethylene, polypropylene, ABS copolymer, cellulose acetate. The thermosetting plastics which may be mentioned, among others, are phenol-formaldehyde, urea-formaldehyde, polyurethane, epoxy, and silicone. The methods of manufacture of some of these polymeric foams are given below.

2.17.1 Rigid Foam Blowing Agents

There are four types of polymers typically used for rigid foam production, namely, polystyrene, polyurethane, polyolefin, and phenolic. Within the polyolefin segment, rigid foams can be produced using polyethylene or polypropylene. Following the implementation of the Montreal Protocol, chlorofluorocarbons (CFC-11 and CFC-12) which had been the primary blowing agents for both flexible and rigid foams, were no longer available. Hydrochlorofluorocarbons (HCFCs) were one of the primary blowing agents that were then adopted, specifically HCFC-141b, HCFC-142b, and HCFC-22. Insulating foam products (with some exceptions) generally utilize HCFCs due to the superior insulation properties that they impart. The non-ozone depleting (i.e., not CFCs or HCFCs) blowing agents that are currently in use and will be substituted for HCFCs as the latter are phased out are: (i) hydrofluorocarbons (HFCs); (ii) hydrocarbons (e.g., pentanes, butanes); and (iii) carbon dioxide.

Non-insulating foam products typically utilize hydrocarbons, such as isobutane, pentane, isopentane, and hexane. The use of CO₂ (either water-based or liquid) is a major identified option to reduce the emission of non-HCFC blowing agents from polyurethane foam and extruded polystyrene boardstock applications. However, the thermal insulation properties of CO₂-blown foam are significantly compromised when compared to halocarbon-blown foam. Halocarbons (i.e., HCFCs, HFCs) are thus expected to be used in insulation foam manufacture for several years into the future. The primary HCFC replacements in these sectors are expected to be the liquid HFCs, which may see extensive use once HCFCs can no longer be used.

2.17.2 Polystyrene Foams

Polystyrene, widely used in injection and extrusion molding, is also extensively used in the manufacture of plastic foams for a variety of applications. Polystyrene produces light, rigid, closed-cell plastic foams

having low thermal conductivity and excellent water resistance, meeting the requirements of low-temperature insulation and buoyancy applications. Two types of low-density polystyrene foams are available to the fabricator, molder, or user: (1) extruded polystyrene foam and (2) expandable polystyrene for molded foam.

2.17.2.1 Extruded Polystyrene Foam

This material is manufactured as billets and boards by extruding molten polystyrene containing a blowing agent (nitrogen gas or chemical blowing agent) under elevated temperature and pressure into the atmosphere where the mass expands and solidifies into a rigid foam. Many sizes of extruded foam are available, some as large as 10 in. \times 24 in. \times 9 ft. The billets and boards can be used directly or cut into different forms. One of the largest markets for extruded polystyrene in the form of boards is in low-temperature insulation (e.g., truck bodies, railroad cars, refrigerated pipelines, and low-temperature storage tanks for such things as liquefied natural gas). Another growing market for extruded polystyrene boards is residential insulation. Such boards are also used as the core material for structural sandwich panels, used prominently in the construction of recreational vehicles.

2.17.2.2 Expandable Polystyrene

Expandable polystyrene is produced in the form of free-flowing pellets or beads containing a blowing agent. Thus, pellets chopped from an ordinary melt extruder or beads produced by suspension polymerization are impregnated with a hydrocarbon such as pentane. Below 70°F (21°C) the vapor pressure of the pentane dissolved in the polymer is low enough to permit storage of the impregnated material (expandable polystyrene) in a closed container at ordinary temperature and pressure. Even so, manufacturers do not recommend storing for more than a few months.

The expandable polystyrene beads may be used in a tubular blow-extrusion process (Figure 2.59) to produce polystyrene foam sheet, which can subsequently be formed into containers, such as egg cartons and cold-drink cups, by thermoforming techniques.

Expandable polystyrene beads are often molded in two separate steps: (1) Preexpansion or prefoaming of the expandable beads by heat, and (2) further expansion and fusion of the preexpanded beads by heat in the enclosed space of a shaping mold.

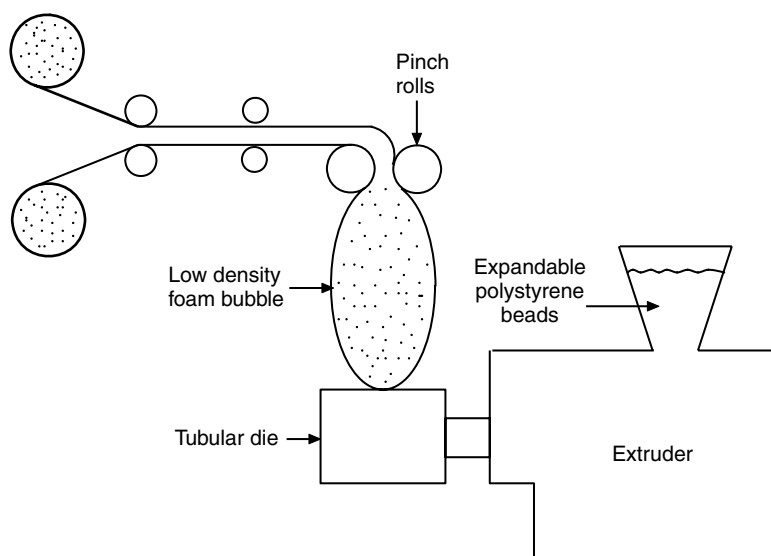


FIGURE 2.59 Tubular blow extrusion for production of low-density polystyrene foam sheet.

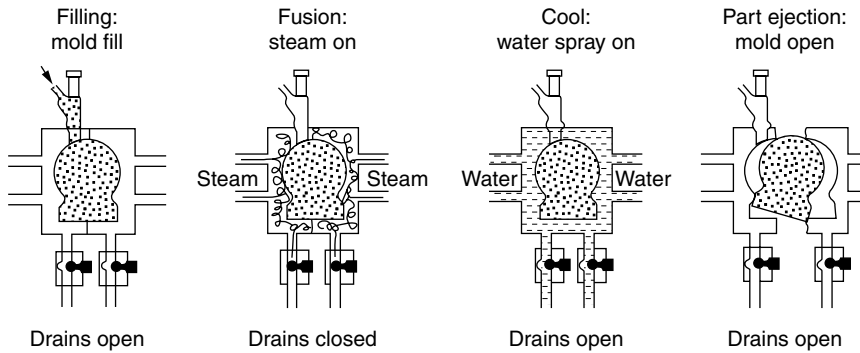


FIGURE 2.60 Molding of preexpanded (prefoamed) polystyrene beads. (Adapted from *PELASPAN Expandable Polystyrene*, Form 171-414, Dow Chemical Co., 1966.)

Steam heat is used for preexpansion in an agitated drum with a residence time of a few minutes. As the beads expand, a rotating agitator prevents them from fusing together, and the preexpanded beads, being lighter, are forced to the top of the drum and out the discharge chute. They are then collected in storage bins for aging prior to molding. The usual lower limit of bulk density for bead preexpansion is 1.0 lb/ft.^3 (0.016 g/cm^3), compared to the virgin bead bulk density of about 35 lb/ft.^3 (0.56 g/cm^3).

Molding of preexpanded (prefoamed) beads requires exposing them to heat in a confined space. In a typical operation (Figure 2.60) prefoamed beads are loaded into the mold cavity, the mold is closed, and steam is injected into the mold jacket. The prefoamed beads expand further and fuse together as the temperature exceeds T_g . The mold is cooled by water spray before removing the molded article. Packages shaped to fit their contents (small sailboats, toys, drinking cups, etc.) are made in this way. Special machines have been designed to produce thin-walled polystyrene foam cups. Very small beads at a prefoamed density of approximately $4\text{--}5 \text{ lb/ft.}^3$ ($0.06\text{--}0.08 \text{ g/cm}^3$) are used, which allow easy flow into the molding cavity and produce a cup having the proper stiffness for handling.

2.17.2.3 Structural Foams

Structural foam is the term usually used for foam produced in an injection molding press and made of almost many thermoplastic resin. Structural foam is always produced with a hard integral skin on the outer surfaces and a cellular core in the interior, and is used almost exclusively for production of molded parts. The process is thus ideally suited for fabrication of parts such as business machine housings (commonly for ABS), and similar parts or components in which lightweight and stiffness are required.

The structural foam injection molding process (Figure 2.61), by which a product with a cellular core and a solid skin can be molded in a single operation, gets its name from the application of its product rather than the mechanism of the process itself. In a manner directly opposite to the vented extruder (Figure 2.21), a blowing agent, often nitrogen, is injected into the melt in the extruder. The polymer melt, injected with gas, is then forced into the accumulator where it is maintained at a pressure and temperature high enough to prevent foaming (Figure 2.61a). When a sufficient charge has accumulated it is transferred into the mold (Figure 2.61b). The melt foams and fills the mold at a relatively low pressure ($1.3\text{--}2.6 \text{ MPa}$) compared to the much higher pressure in the accumulator. The lower operating pressures of the molds make the molds less expensive than those used for conventional injection molding. However, the cycle times are longer because the foam being a good insulator, takes longer time to cool.

Structural foams can also be made using a chemical blowing agent (discussed later) rather than an inert gas. In that case, a change in pressure or temperature on entering the mold triggers gas formation. Today structural foam injection molding is a very fast-growing polymer processing technique that can be used to modify the properties of thermoplastics to suit specific applications.

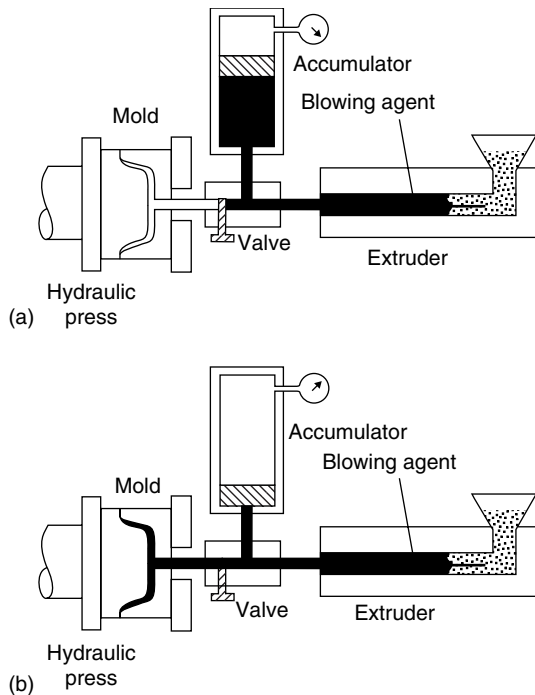


FIGURE 2.61 Structural foam process. (a) Filling the accumulator. The blowing agent (usually nitrogen) is injected into the melt in the extruder before it is passed into the accumulator. (b) Filling the mold. The accumulator ram injects the melt into the mold where the reduced pressure allows the gas to foam the resin.

2.17.3 Polyolefin Foams

Polyolefin foams can be produced with closely controlled density and cell structure. Generally the mechanical properties of polyolefins lies between those of a rigid and a flexible foam. Polyolefin foams have a very good chemical and abrasion resistance as well as good thermal insulation properties. Cross-linking improves foam stability and polymer properties.

A variety of foams can be produced from various types of polyethylenes and cross-linked systems having a very wide range of physical properties, and foams can be tailor-made to a specific application. Polypropylene has a higher thermostability than polyethylene. The production volume of polyolefin foams is not as high as that of polystyrene, polyurethane, or PVC foams. This is due to the higher cost of production and some technical difficulties in the production of polyolefin foams. The structural foam injection molding process, described previously for polystyrene, is also used for polyethylene and polypropylene structural foams (see Figure 2.61).

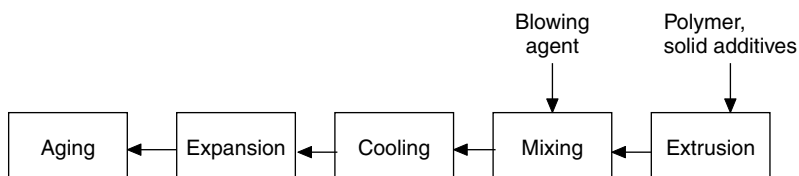


FIGURE 2.62 Block diagram of polyolefin foam manufacture by extrusion process.

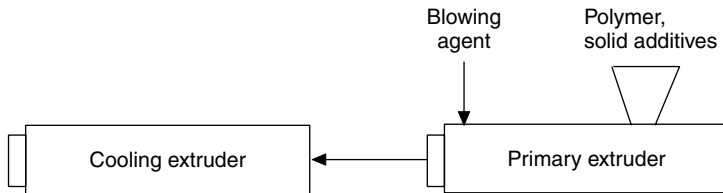


FIGURE 2.63 Schematic diagram of tandem extruder.

Commercial extrusion processes for polyolefin foam products are derived from the original Dow process which basically involves five steps, namely, extrusion, mixing, cooling, expansion, and aging (see [Figure 2.62](#)). These steps of the extrusion process may be performed on equipment of several different configurations such as single-screw extruders, twin-screw extruders, and tandem-extruder lines. Single-screw extruders must be equipped with a multistage long screw of high length-to-diameter ratio capable of performing all the aforesaid extrusion steps. Twin-screw extruders, on the other hand, have low shear rate and high mixing ability both of which are desirable in foam extrusion.

Except where the extrusion rate is low such as for products having a small cross-section, most polyolefin foam products are made with tandem-type extruders, as shown in [Figure 2.63](#). The primary extruder consisting of a two-stage screw melts the resin and then mixes the melt with the solid additives and liquid blowing agent, whereas the second extruder, usually larger than the primary one and designed to provide maximum cooling efficiency, cools the molten polymer mixture to the optimum foaming temperature. In some equipment, however, the second extruder is designed to perform both as mixer for the blowing agent and as cooler.

An alternative to large tandem extruders is the accumulating extrusion system which provides a high instantaneous extrusion rate. It is commonly employed for producing large plank products. In the simple system, shown in [Figure 2.64](#), the foamable melt is fed into an accumulator by a single screw extruder and pushed out by a ram through a die orifice. The process is discontinuous, resulting in a loss of yield, but it has the advantage of low capital requirement.

The shape of a polyolefin foam product is determined largely by the shape of the die. Thus a circular die is used for a rod, an annular die for a tube or sheet product, and a slit die for a plank product. To make

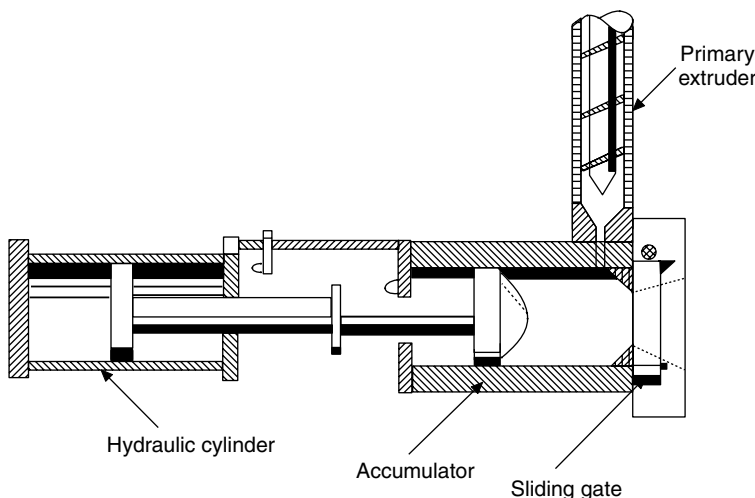


FIGURE 2.64 Schematic of accumulation extrusion system.

polyolefin foam sheet, the extruded tubular foam, expanding at the annular die, is guided over a sizing mandrel, slit, laid flat, and wound into a roll [33]. Cool air is blown in at the nose of the mandrel to reduce the friction between the hot expanding foam and the mandrel.

The extruded polyolefin foam must be dimensionally stabilized by aging, since the foam deforms according to the internal cell pressure, which changes with time as air and gaseous blowing agent diffuse into and out of the foam at different rates. If the rates are equal, the cell pressure, and hence the foam dimensions, will remain constant, as is found for the LDPE/CDC-114 system. Most blowing agents, however, permeate through polyolefins faster than air and, as a result, the foams shrink. The aging time required for the shrunken foam to recover and stabilize depends on the properties of the polymer and the physical attributes of the foam, such as the open-cell content, foam density, and foam thickness. The aging time may range from less than a week for a thin sheet to several weeks for a thick plank.

The production line of a typical process to manufacture thin ultra-low-density (ULD) polypropylene foam sheet, consists of tandem extruders, an accumulating vessel, and an annular die. The secondary extruder is designed to mix a large amount of blowing agent into the polymer and then to cool the mixture. The blowing agent consists of a large proportion (90%) of a highly soluble blowing agent such as CFC-11 which provides the heat sink necessary for foam stabilization and a small proportion (10%) of a low-permeability blowing agent such as CFC-12 or CFC-114 which serves as an inflatant. The accumulating extrusion system allows the high extrusion rate required for the production of ULD foam sheet.

There are several processes for the production of moldable polyolefin beads. In the BASF process, LDPE foam strands are extruded out of a multi-hole die and granulated to beads by a die-face cutter. Inexpensive butane is used as the blowing agent and the foam beads are then cross-linked by electron-beam. As the beads have atmospheric cell pressure, a special technique is required to develop the necessary cell pressure for molding [34].

In the Kanegafuchi process, most widely used to manufacture LDPE foam beads, dicumyl peroxide is impregnated into finely pelletized LDPE beads suspended in water in an autoclave with the help of a dispersant such as basic calcium tertiary phosphate and sodium dodecylbenzene sulfonate. The beads are then heated to cross-link. The cross-linked beads are impregnated with a blowing agent (e.g., CFC-12), cooled, discharged from the autoclave and immediately expanded with steam to make foam beads. For molding, the foam beads are charged into a mold and heated with superheated steam (>140 kPa) to expand and weld.

The majority of cross-linked polyolefin foam sheet products are made by one of the four Japanese processes: Sekisui, Toray, Furukawa, and Hitachi, the first two of which use the radiation method and the latter two a chemical method for cross-linking.

The flow diagram of the radiation cross-linked polyolefin foam sheet process is shown in Figure 2.65. The key steps of the process include a uniform mixing of polymer and blowing agent (powder), manufacturing void-free sheet of uniform thickness, cross-linking the sheet to the desired degree by irradiation with a high-energy ray, and then softening and expanding the sheet in a foaming chamber

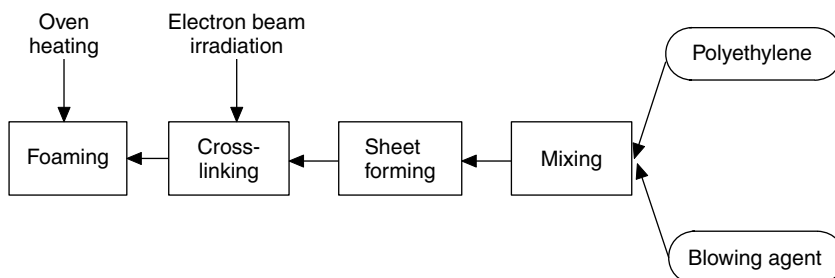


FIGURE 2.65 Flow diagram of radiation cross-linked polyolefin foam sheet forming process.

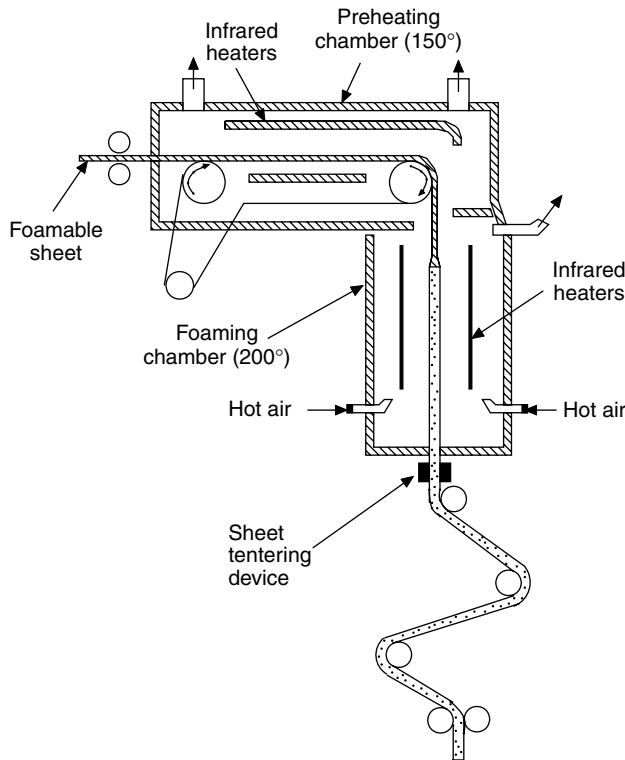


FIGURE 2.66 Schematic of Sekisui vertical foaming oven for cross-linked polyolefin foam sheet.

(oven) using a suitable support mechanism. The Sekisui process employs a vertical air oven like the one shown in Figure 2.66 for expanding the foamable sheet. The oven consists of a horizontal preheating chamber and a vertical foaming chamber. The rapidly expanding sheet supports itself by gravity in the vertical direction, while a specially designed tentering device keeps the sheet spread out. In the Toray process, the foamable sheet is expanded while afloat on the surface of molten salts. The process is suitable for producing cross-linked PP foam sheet as well as PE foam sheet.

The flow diagram of the chemically cross-linked polyolefin foam sheet process is shown in Figure 2.67. Unlike in the radiation cross-linking process, a peroxide cross-linking agent is incorporated in the polymer along with the blowing agent. Therefore, a tighter temperature control must be maintained in the sheet manufacturing steps to prevent premature cross-linking by the peroxide. In the oven, on the other hand, the cross-linking of the polyolefin sheet must be thermally effected without causing the

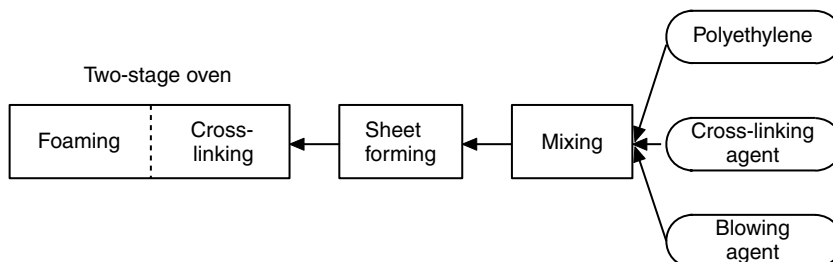


FIGURE 2.67 Flow diagram of chemically cross-linked polyolefin foam sheet forming process.

blowing agent to decompose. Consequently, both the oven design and the selection of raw materials are more difficult in the chemical cross-linking process. Both the Furukawa and Hitachi processes employ horizontal air ovens consisting of at least two sections, the preheating section and the foaming/forming section, and having one or more non-stick conveyors to support the sheet during heating and expansion [33].

Polyolefin foams have many and varied applications due to their unique properties which include buoyancy, resiliency, energy absorption, low thermal conductivity, resistance to chemicals, thermoformability, and ease of fabrication. The major application areas of polyolefin foams are cushion packaging (pads and saddles, encapsulation, case inserts, etc.), construction (expansion joint filler, closure strips, floor underlayment etc.), automotive (headliner, door trim, instrument panel, trunk liner, air conditioner liner, etc.), insulation (insulation of pipe, storage tanks), and sports and leisure (life vests, surfboards, swim aids, ski belts, gym mats, etc.). Thin polyolefin foam sheet products are used primarily as wrapping materials to protect the surfaces of articles from minor dents and abrasion during handling and shipping.

2.17.4 Polyurethane Foams

Polyurethane foams, also known as urethane foams or U-foams, are prepared by reacting hydroxyl-terminated compounds called polyols with an isocyanate (see [Figure 1.29](#)). Isocyanates in use today include toluene diisocyanate, known as TDI, crude methylenebis(4-phenyl-isocyanate), known as MDI, and different types of blends, such as TDI/crude MDI. Polyols, the other major ingredient of the urethane foam, are active hydrogen-containing compounds, usually polyester diols and polyether diols.

It is possible to prepare many different types of foams by simply changing the molecular weight of the polyol, since it is the molecular backbone formed by the reaction between isocyanate and polyol that supplies the reactive sites for cross-linking ([Figure 1.29](#)), which in turn largely determines whether a given foam will be flexible, semirigid, or rigid. In general, high-molecular-weight polyols with low functionality produce a structure with a low amount of cross-linking and, hence, a flexible foam. On the other hand, low-molecular-weight polyols of high functionality produce a structure with a high degree of cross-linking and, consequently, a rigid foam. Of course, the formulation can be varied to produce any degree of flexibility or rigidity within these two extremes.

The reactions by which urethane foam are produced can be carried out in a single stage (one-shot process) or in a sequence of several stages (prepolymer process and quasi-prepolymer process.) These variations led to 27 basic types of products or processes, all of which have been used commercially.

In the one-shot process, all of the ingredients—*isocyanate, polyol, blowing agent, catalyst, additives, etc.*—are mixed simultaneously, and the mixture is allowed to foam. In the prepolymer method ([Figure 1.29](#)), a portion of the polyol is reacted with an excess of isocyanate to yield a prepolymer having isocyanate end groups. The prepolymer is then mixed with additional polyol, catalyst, and other additives to cause foaming. The quasi-prepolymer process is intermediate between the prepolymer and one-shot processes.

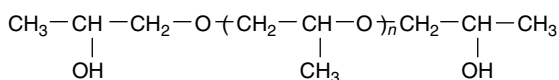
2.17.4.1 Flexible Polyurethane Foams

The major interest in flexible polyurethane foams is for cushions and other upholstery materials. Principal market outlets include furniture cushioning, carpet underlay, bedding, automotive seating, crash pads for automobiles, and packaging. The density range of flexible foams is usually 1–6 lb/ft.³ (0.016–0.096 g/cm³). The foam is made in continuous loaves several feet in width and height and then sliced into slabs of desired thickness.

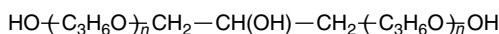
2.17.4.1.1 One-Shot Process

The bulk of the flexible polyurethane foam is now being manufactured by the one-shot process using polyether-type polyols because they generally produce foams of better cushioning characteristics. The main components of a one-shot formulation are polyol, isocyanate, catalyst, surfactant, and blowing agent.

Today the bulk of the polyether polyols used for flexible foams are propylene oxide polymers. The polymers prepared by polymerizing the oxide in the presence of propylene glycol as an initiator and a caustic catalyst are diols having the general structure



The polyethers made by polymerizing propylene oxide using trimethylol propane, 1,2,6-hexanetriol, or glycerol as initiator are polymeric triols. For example, glycerol gives



The higher hydroxyl content of these polyethers leads to foams of better loadbearing characteristics. Molecular weight in the range 3,000–3,500 is found to give the best combination of properties.

The second largest component in the foam formulation is the isocyanate. The most suitable and most commonly used isocyanate is 80:20 TDI—i.e., 80:20 mixture of tolylene-2,4-diisocyanate and tolylene-2,6-diisocyanate.

One-shot processes require sufficiently powerful catalysts to catalyze both the gas evolution and chain extension reaction (Figure 1.29). Use of varying combinations of an organometallic tin catalyst (such as dibutyltin dilaurate and stannous octoate) with a tertiary amine (such as alkyl morpholines and triethylamine), makes it possible to obtain highly active systems in which foaming and cross-linking reactions could be properly balanced.

The surface active agent is an essential ingredient in formulations. It facilitates the dispersion of water (see below) in the hydrophobic resin by decreasing the surface tension of the system. In addition, it also aids nucleation, stabilizes the foam, and regulates the cell size and uniformity. A wide range of surfactants, both ionic and nonionic, have been used at various times. Commonly used among them are the water-soluble polyether siloxanes.

Water is an important additive in urethane foam formulation. The water reacts with isocyanate to produce carbon dioxide and urea bridges (Figure 1.29). An additional amount of isocyanate corresponding to the water present must therefore be incorporated in the foaming mix. The more water that is present, the more gas that is evolved and the greater number of active urea points for cross-linking. This results in foams of lower density but higher degree of cross-linking, which reduces flexibility. So when soft foams are required, a volatile liquid such as trichloromonofluoromethane (bp 23.8°C) may be incorporated as a blowing agent. This liquid will volatilize during the exothermic urethane reaction and will increase the total gas in the foaming system, thereby decreasing the density,

TABLE 2.2 Urethane One-Shot Foam Formulation

Ingredient	Parts by Weight
Poly(propylene oxide), mol. wt. 2000 and 2OH/molecule	35.5
Poly(propylene oxide) initiated with trifunctional alcohol, mol. wt. 3000 and 3 OH/molecule	35.5
Toluene diisocyanate (80:20 TDI)	26.0
Dibutyltin dilaurate	0.3
Triethylamine	0.05
Water	1.85
Surfactant (silicone)	0.60
Trichloromonofluoromethane (CCl ₃ F)	12.0
Final density of foam = 1.4 lb/ft. ³ or 0.022 g/cm ³ (2.0 lb/ft. ³ or 0.032 g/cm ³ if CCl ₃ F is omitted)	

Source: One-Step Urethane Foams, 1959. Bull, F40487, Union Carbide Corp.

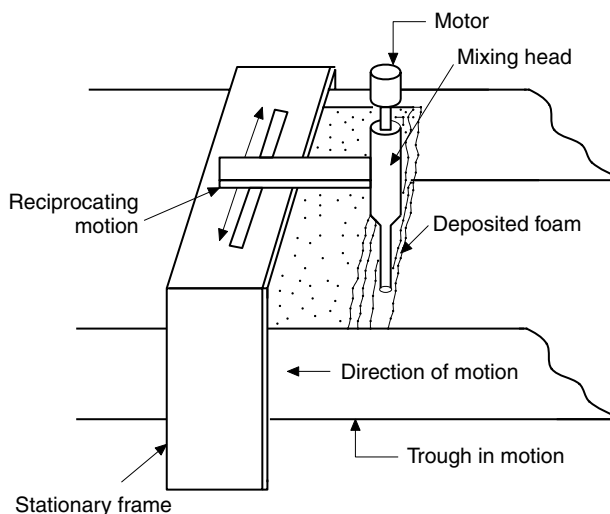


FIGURE 2.68 Schematic of a Hanecke-type machine for production of polyurethane foam in block form by one-shot process.

but it will not increase the degree of cross-linking. However, where it is desired to increase the cross-link density independently of the isocyanate-water reaction, polyvalent alcohols, such as glycerol and pentaerythritol, and various amines may be added as additional cross-linking agents. A typical formulation of one-shot urethane foam system is shown in [Table 2.2](#)

Most foam is produced in block form from Hanecke-type machines (Figure 2.68) or some modification of them. In this process [35], several streams of the ingredients are fed to a mixing head which oscillates in a horizontal plane. In a typical process, four streams may be fed to the mixing head: e.g., polyol and fluorocarbon (if any); isocyanate; water, amine, and silicone; and tin catalyst. The reaction is carried out with slightly warmed components. Foaming is generally complete within a minute of the mixture emerging from the mixing head. The emergent reacting mixture runs into a trough, which is moving backward at right angles to the direction of traverse of the reciprocating mixing head. In this way the whole trough is covered with the foaming mass.

Other developments of one-shot flexible foam systems include direct molding, where the mixture is fed into a mold cavity (with or without inserts such as springs, frames, etc.) and cured by heat. In a typical application, molds would be filled and closed, then heated rapidly to 300°F–400°F (149°C–204°C) to develop maximum properties.

A good deal of flexible urethane foam is now being made by the cold-cure technique. This involves more reactive polyols and isocyanates in special foaming formulations which would cure in a reasonable time to their maximum physical properties without the need for additional heat over and above that supplied by the exothermic reaction of the foaming process.

Cold-cure foaming is used in the production of what is known as high-resilient foams having high sag factor (i.e., ratio of the load needed to compress foam by 65% to the load needed to compress foam by 25%), which is most important to cushioning characteristics. True cold-cure foams will produce a sag factor of 3–3.2, compared to 2–2.6 for hot-cured foams.

2.17.4.1.2 Prepolymer Process

In the prepolymer process the polyol is reacted with an excess of isocyanate to give an isocyanate-terminated prepolymer which is reasonably stable and has less handling hazards than free isocyanate. If water, catalysts, and other ingredients are added to the product, a foam will result. For better load-bearing and cushioning properties, a low-molecular-weight triol, such as glycerol and trimethylolpropane, is added to the polyol before it reacts with the isocyanate. The triol provides a site for chain branching.

Although the two-step prepolymer process is less important than the one-shot process, it has the advantage of low exotherms, greater flexibility in design of compounds, and reduced handling hazards.

2.17.4.1.3 Quasi-Prepolymer Process

In the quasi-prepolymer process a prepolymer of low molecular weight and hence low viscosity is formed by reacting a polyol with a large excess of isocyanate. This prepolymer, which has a large number of free isocyanate groups, is then reacted at the time of foaming with additional hydroxy compound, water, and catalyst to produce the foam. The additional hydroxy compound, which may be a polyol or a simple molecule such as glycerol or ethylene glycol, also functions as a viscosity depressant. The system thus has the advantage of having low-viscosity components, compared to the prepolymer process, but there are problems with high exotherms and a high free-isocyanate content.

Quasi-prepolymer systems based on polyester polyols and polyether polyols are becoming important in shoe soling, the former being most wear resistant and the latter the easiest to process.

2.17.4.2 Rigid and Semirigid Foams

The flexible foams discussed in previous sections have polymer structures with low degrees of cross-linking. Semirigid and rigid forms of urethane are products having higher degree of cross-linking. Thus, if polyols of higher functionality—i.e., more hydroxyl groups per molecule—are used, less flexible products may be obtained, and in the case of polyol with a sufficiently high functionality, rigid foams will result.

The normal density range for rigid and semirigid foams is about 1–3 lb/ft.³ (0.016–0.048 g/cm³). Some packaging applications, however, use densities down to 0.5 lb/ft.³ (0.008 g/cm³); for furniture applications densities can go as high as 20–60 lb/ft.³ (0.32–0.96 g/cm³), thus approaching solids. At densities of from 2 lb/ft.³ (0.032 g/cm³) to 12 lb/ft.³ (0.19 g/cm³) or more, these foams combine the best of structural and insulating properties.

Semirigid (or semiflexible) foams are characterized by low resilience and high energy-absorbing characteristics. They have thus found prime outlet in the automotive industry for applications like safety padding, arm rests, horn buttons, etc. These foams are cold cured and involve special polymeric isocyanates. They are usually applied behind vinyl or ABS skins. In cold curing, the liquid ingredients are simply poured into a mold in which vinyl or ABS skins and metal inserts for attachments have been laid. The liquid foams and fills the cavity, bonding to the skin and inserts. Formulations and processing techniques are also available to produce self-skinning semirigid foam in which the foam comes out of the mold with a continuous skin of the same material.

Rigid urethane foams have outstanding thermal insulation properties and have proved to be far superior to any other polymeric foam in this respect. Besides, these rigid foams have excellent compressive strength, outstanding buoyancy (flotation) characteristics, good dimensional stability, low water absorption, and the ability to accept nails or screws like wood. Because of these characteristics, rigid foams have found ready acceptance for such applications as insulation, refrigeration, packaging, construction, marine uses, and transportation.

For such diverse applications several processes are now available to produce rigid urethane foam. These include foam-in-place (or pour-in-place), spraying, molding, slab, and laminates (i.e., foam cores with integral skins produced as a single unit). One-shot techniques can be used without difficulty, although in most systems the reaction is slower than with the flexible foam, and conditions of manufacture are less critical. Prepolymer and quasi-prepolymer systems were also developed in the United States for rigid and semirigid foams, largely to reduce the hazards involved in handling TDI where there are severe ventilation problems.

In the foam-in-place process a liquid urethane chemical mixture containing a fluorocarbon blowing agent is simply poured into a cavity or metered in by machine. The liquid flows to the bottom of the cavity and foams up, filling all cracks and corners and forming a strong seamless core with good adhesion to the inside of the walls that form the cavity. The cavity, of course, can be any space, from the space

between two walls of a refrigerator to that between the top and bottom hull of a boat. However, if the cavity is the interior of a closed mold, the process is known as molding.

Rigid urethane foam can be applied by spraying with a two-component spray gun and a urethane system in which all reactants are incorporated either in the polyol or in the isocyanate. The spraying process can be used for applying rigid foam to the inside of building panels, for insulating cold-storage rooms, for insulating railroad cars, etc.

Rigid urethane foam is made in the form of slab stock by the one-shot technique. As in the Henecke process (Figure 2.61), the reactants are metered separately into a mixing head where they are mixed and deposited onto a conveyor. The mixing head oscillates in a horizontal plane to insure an even deposition. Since the foaming urethane can structurally bond itself to most substrates, it is possible (by metering the liquid urethane mixture directly onto the surface skin) to produce board stock with integral skins already attached to the surface of the foam. Sandwich-construction building panels are made by this technique.

2.17.5 Foamed Rubber

Although foamed rubber and foamed urethanes have many similar properties, the processes by which they are made differ radically. In a simple process a solution of soap is added to natural rubber (NR) latex so that a froth will result on beating. Antioxidants, cross-linking agents, and a foam stabilizer are added as aqueous dispersions.

Foaming is done by combined agitation and aeration with automatic mixing and foaming machines. The stabilizer is usually sodium silicofluoride (Na_2SiF_6). The salt hydrolyzes, yielding a silica gel which increases the viscosity of the aqueous phase and prevents the foam from collapsing. A typical cross-linking agent is a combination of sulfur and the zinc salt of mercaptobenzothiazole (accelerator). Cross-linking (curing or vulcanization) with this agent takes place in 30 min at 100°C.

When making a large article such as a mattress, a metal mold may be filled with the foamed latex and heated by steam at atmospheric pressure. After removing the foamed rubber article from the mold, it may be dewatered by compressing it between rolls or by centrifuging and by drying with hot air in a tunnel dryer. In foamed rubber formulation a part of the NR latex can be replaced by a synthetic rubber latex. One such combination is shown in Table 2.3.

2.17.6 Epoxy Resins

Any epoxy resin can be made foamable by adding to the formulation some agent that is capable of generating a gas at the curing temperature prior to gelation. Such foaming agents may be low-boiling liquids which vaporize on heating (e.g., CFCs such as Freons) or blowing agents that liberate a gas when heated above 70°C, such as 2,2'-azobis(isobutyronitrile) or sulfonylhydrazide, which decompose evolving

TABLE 2.3 Foamed Rubber Formulation

Ingredient	Parts by Weight
Styrene-butadiene latex (65% solids)	123
Natural rubber latex (60% solids)	33
Potassium oleate	0.75
Sulfur	2.25
Accelerators	
Zinc diethyldithiocarbamate	0.75
Zinc salt of mercaptobenzothiazole	1.0
Trimene base (reaction product of ethyl chloride, formaldehyde, and ammonia)	0.8
Antioxidant (phenolic)	0.75
Zinc oxide	3.0
Na_2SiF_6	2.5

Source: Stern, H. J. 1967. *Rubber: Natural and Synthetic*, Palmerton, New York.

nitrogen. A foaming gas can also be generated in situ by adding a blowing agent that reacts with amine (curing agent) to form the gas. A typical such system consists of an epoxy resin, a primary amine (hardener), and a hydrogen-active siloxane (blowing agent). The siloxane reacts with the amine, evolving hydrogen as a foaming gas.

Instead of using amines it is also possible to use other hydrogen-active hardeners such as phenols and carboxylic acids. The reaction of gas evolution occurs immediately after mixing resin and hardeners and before the mixture begins to cure in the mold. This is essential for the formation of closed-cell foam structure during the curing, which takes place under a definite expansion pressure against the mold wall, leading to formation of dense casting. In the production of expanded laminates of sandwich configuration, this yields very tough and impact-resistant structures.

Expanded materials with excellent high-temperature properties are obtained when cresol novolacs are used as hardeners. A typical formulation is based on mixtures of bisphenol A resins and epoxy novolac resins which are cured by cresol novolacs and accelerated by suitable nitrogen-containing agents.

Applications of epoxy foams can be categorized in three areas, namely, (1) unreinforced materials, (2) glass-fiber-reinforced materials, and (3) sandwich constructions [33]. Because of their light weight and absence of shrinkage, foamed epoxies are used in the production of large-scale patterns. Having excellent dielectric properties, epoxy foams find applications in electronics such as for casting and sealing electronic components like small transformers and capacitors, and in insulating cables.

The light weight properties of foamed epoxies are utilized in fiber-reinforced materials for which glass fiber mats and unidirectional rovings are most suitable, with the majority of applications involving sandwich constructions. A few practical examples are foamed epoxy windsurfing board, epoxy rotor blades for wind energy generators, and automotive spoilers.

2.17.7 Urea-Formaldehyde Foams

Urea-formaldehyde (UF) foams are basically two-component systems as the production of the foams requires mainly a UF resin and a foam stabilizing agent. The UF resin (see [Chapter 4](#)) is produced by the condensation of urea and formaldehyde in the range of mole ratios of 2: 3–1: 2 in the presence of alkaline catalysts ($\text{pH} \sim 8$), which yield only short-chain oligomers, and under weakly acidic conditions ($\text{pH} 4\text{--}6$), which result in a higher molecular weight mixture of oligomers (solubilized by attached methylol groups). Though numerous substances have been proposed as foam-stabilizing agents for the commercial foam system, aqueous solutions of the sodium salts of dodecylbenzene sulfonic acid and dibutyl-naphthalene sulfonic acid have proven to be of value. Aqueous solutions of strongly dissociating organic and inorganic acids with a pH range of 1–1.5 are used as hardening agents. However, phosphoric acid is preferred because of its negligible corrosive action. The hardening agent is preferentially added to the foam stabilizing agent and the concentration of the hardener is chosen so that the final foam gels within 30–90 sec at 20–25°C after mixing the components.

In a stationary process for making UF foams, a mixture of water and foam-stabilizing agent is introduced into a vessel equipped with tubular vanes. Foaming takes place upon feeding air and a urea-formaldehyde resin solution (see “Urea-Formaldehyde Resin” in [Chapter 5](#)). The generated foam is guided by the action of the tubular vanes to the outlet channel of the vessel from where the foam exits as a rectangular slab and is transported on a conveyor belt until the foam structure hardens sufficiently. Blocks are cut from the foam slab, dried at about 40°C for about 2 h, and then pressed mechanically into sheets of the required dimensions [33].

For on-site production of foam, the raw materials are transported by pumps into a foaming machine. A dispersion of foam stabilizing agent is formed in water in the machine and the resin is introduced into the mixing chamber through jets. The finished foam emerges from the plastic pipe and can be used immediately at the site. One thousand liters (1 m^3) of foam can be produced on-site from 20 liters of resin and 18 liters of foam solution.

The UF foam plastics are open-cell cellular materials with the capability of absorbing oils and solvents. UF foam is non-toxic, nonflammable, and stable with respect to almost all organic solvents, light and

heavy mineral oils, but is decomposed by dilute and concentrated acids and alkalis. It exhibits extraordinary aging stability, has good sound-absorbing properties, and has the lowest thermal conductivity, despite the open cells. These properties coupled with its light weight (bulk density 11 kg/m³) and low manufacturing cost, make UF foam suitable for a wide spectrum of applications, including industrial filling materials, insulating in enclosed cavities, plant substrates (soil-free cultivation), and medical applications.

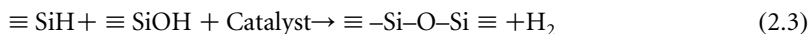
UF foam is used on-site to fill cavities of all shapes and sizes, whether of natural origin or resulting from construction wall or other applications. It has been successfully employed in mining for over 50 years. The complete filling of cavities eliminates the hazard of methane accumulation and reduces the danger of fire and explosion. UF foam filling is an inexpensive, rapid, and excellent heat-insulated lightweight construction method. When insulation is retrofitted, the foam is introduced into the existing cavities through sealable small holes.

When UF foam is formed, formaldehyde is released. It is important to make sure that the proper ratio of components is employed and suitable construction measures are taken, as otherwise the problems of formaldehyde release from foam over short term or long term may be encountered. With present day technologies, it is possible to satisfy strict conditions that a formaldehyde level of 0.1 ppm should not be exceeded in the air of a room used continuously for dwelling purposes.

Geo- and hydroponics, as well as *plastoponics* are terms referring to the cultivation and breeding of plants with foam as flakes or in solid form. Beans, potatoes, carrots, tomatoes and ornamental plants have been grown extensively in foam. Its suitability for land recovery in desert and semi-desert regions has been established through extensive testing.

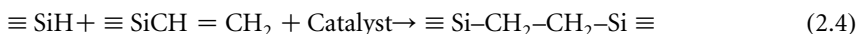
2.17.8 Silicone Foams

Silicone foams result from the condensation reaction between $\equiv\text{SiH}$ and $\equiv\text{SiOH}$ shown below:



When these three components (that is, $\equiv\text{SiH}$ -containing cross-linker, $\equiv\text{SiOH}$ -containing polymer, and catalyst) are mixed together, both blowing (generation of hydrogen gas) and curing or cross-linking, that is, formation of siloxane linkage ($\equiv\text{Si-O-Si}\equiv$) occur. It should be noted, however, that a cross-linked product forms if the functionality of the $\equiv\text{SiH}$ -containing component is 3 or greater and the $\equiv\text{SiOH}$ -containing compound has a functionality of at least 2. These reactions are heat accelerated, but they occur readily at room temperature in the presence of catalyst. These RTV (room temperature vulcanizing) foams are thus two-pack systems. Generally, the $\equiv\text{SiH}$ (such as methylhydrogen siloxane) and catalyst make up the second component. A variety of catalysts can be used to promote the reaction. Chloroplatinic acid or other soluble platinum compound is most commonly used because it imparts flame retardancy to the formulation.

If a vinyl endblocked polymethylsiloxane is used in place of polydimethylsiloxane in the above formulation, then another competing reaction can also occur as shown below:



The reaction is also catalyzed by platinum. The addition of some vinyl-containing polysiloxane can thus improve properties such as density, tensile strength, cure rate, and so forth.

Although hydrogen generation [Equation 2.3] is the most prevalent method of blowing silicone foam, there are other approaches. Adding a gas at a high enough pressure (so its volume is low before it expands) is an easy way to make foam. Gases commonly used are N₂, CO₂, and air-pressurized liquefied gases such as CFCs. One may also use chemical blowing agents (see later), which decompose generating gas when heat is applied or pH is changed. Nitrogen-liberating organic blowing agents are used extensively for foaming silicone gum.

Silicones in general are inert to most environmental agents and have many unique properties (see “Silicones” in Chapter 4). When siloxane polymers are processed into foams they carry with them most of their durability characteristics and characteristic properties. Silicone foams are thus used in a wide range of applications. Flexible foam sheet is used in airplanes as the material for fire blocking, insulation of air ducts, gasketing in engine housing compartments, and shock absorbers. Silicone foam is a popular choice in the construction industry, because of its weatherability, thermal insulation, and sealing capability.

2.17.9 Phenolic Foams

Phenolic foam is a light weight foam created from phenolic resins. It is used in a large range of applications, such as flower foam blocks, building thermal insulation, fire protection, damping, and civil engineering in a wide variety of shapes: blocks, sheets, and sprayed foams.

Phenolic foams are generally made using a resol-type phenolic resin (or a resin blend typically containing 60% of a resol-type resin and 40% of a resorcinol-modified novolac resin), surfactants, blowing agents, catalysts, and additives. Surfactants and additives are mixed into the resin and the blend is then mixed with the liquid blowing agent(s) and finally with an acid catalyst, e.g., H_3PO_4 .

Surfactants are used to control cell size and structure. The most common surfactants are siloxane-oxyalkylene copolymers, polyoxyethylene sorbitan fatty acid esters, and the condensation products of ethylene oxide with castor oil and alkyl phenols. A commonly added additive is urea which is used as a formaldehyde scavenger. Very fine particle size inorganic fillers can be added to act as nucleating sites and to promote finer, more uniform cell structure, as well as increased compressive strength, but at a cost of higher density.

The most common blowing agents used for making phenolic foams are organic liquids that have boiling points approximately in the range 20°C–90°C. Suitable blowing agents include HFCs, HCFCs and others, and hydrocarbons having from about 3–10 carbon atoms such as pentane, hexane and petroleum ether. Hydrocarbons such as isopentane, isobutane and hexane are the preferred blowing agents for flower blocks. In insulating foam sector, however, the non-hydrocarbon blowing agent alternatives are not as viable and Foranil fluorochemical blowing agents have been mainly used for their insulating properties and non-flammability.

Phenolic foams can also be prepared without the use of CFC or hydrocarbon blowing agents. In a typical preparation [37], resol 200, ethoxylated castor oil 8, boric anhydride accelerator 36, and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 36 parts are mixed and heated for about 4 minute at 120°C to obtain a foam having density 0.003 g/cm³ and 29% closed cells. In another method [38], 1 mol phenol, 2.6 mol formaldehyde, and 5% dimethylaminoethanol are heated at 70°C–100°C for 4 h to obtain a liquid (70%–80% solids content) which is mixed with 2%–3% silicone foam regulator and 5 parts NaHCO_3 . Toluenesulfonic acid (20 parts, 80% aq.) is then added to obtain a stable rigid foam.

2.17.10 Poly(Vinyl Chloride) Foams

A number of methods have been devised for producing cellular products from PVC, either by a mechanical blowing process or by one of several chemical blowing techniques. PVC foams are produced in rigid or flexible forms. The greatest interest in rigid PVC foam is in applications where low-flammability requirements prevail. It has an almost completely closed cell structure and therefore low water absorption. The rigid PVC foam is used as the cellular layer of some sandwich and multi-layer panels.

Plastisols are the most widely used route to flexible expanded PVC products. Dolls, gaskets, and resilient covers for tool handles, for example, are produced from expandable plastisol compounds by molding, while varied types of upholstery, garment fabrics, and foam layer in coated-fabric flooring are made from coatings with such compounds. Figure 2.69 shows a schematic representation of the German Trovipor process for producing flexible, mainly open cell, and low to medium density (60–270 kg/m³, 3.75–16.87 lb/ft.³) PVC foam. It is normally produced in the form of continuous sheet (Figure 2.69).

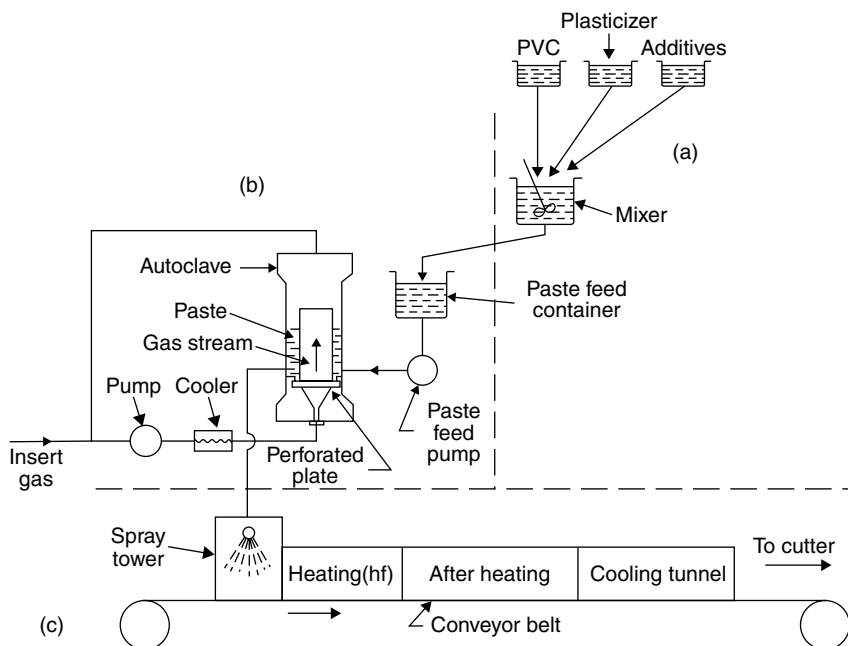


FIGURE 2.69 Schematic representation of the Trovivor process. (a) PVC paste preparation. (b) Gasification of PVC paste. (c) Spraying and fusion.

Many *chemical blowing (foaming) agents* have been developed for cellular elastomers and plastics, which, generally speaking, are organic nitrogen compounds that are stable at normal storage and mixing temperatures but undergo decomposition with gas evolution at reasonably well-defined temperatures. Three important characteristics of a chemical blowing agent are the decomposition temperature, the volume of gas generated by unit weight ("gas number," defined as the volume of gas, in cm^3 , liberated by the transformation of 1 g of the blowing agent per minute), and the nature of the decomposition products. Since nitrogen is an inert, odorless, nontoxic gas, nitrogen-producing organic substances are preferred as blowing agents. Several examples of blowing agents [39] especially recommended for vinyl plastisols are shown in Table 2.4; in each case the gas generated is nitrogen.

To produce uniform cells, the blowing agent must be uniformly dispersed or dissolved in the plastisol and uniformly nucleated. It should decompose rapidly and smoothly over a narrow temperature range corresponding to the attainment of a high viscosity or gelation of the plastisol system. The gelation involves solvation of the resin in plasticizer at 300°F – 400°F (149°C – 204°C), the temperature depending on the ingredients employed in the plastisol. The foam quality is largely determined by the matching of the decomposition of the blowing agent to the gelation of the polymer system. If gelation occurs before gas evolution, large holes or fissures may form. On the other hand, if gas evolution occurs too soon before gelation, the cells may collapse, giving a coarse, weak, and spongy product.

Among the blowing agents listed in Table 2.4, azobisformamide (ABFA) is the most widely used for vinyls because it fulfills the requirements efficiently. ABFA decomposition can also be adjusted through proper choice of metal organic activators so that the gas evolution occurs over a narrow range within the wide range given in Table 2.4.

Though the gas number of ABFA is normally 220 – $260 \text{ cm}^3/\text{g}$, it can go up to $420 \text{ cm}^3/\text{g}$ in the presence of catalysts. Azodicarbonamide is recommended for foaming of PVC, polyolefins, polyamides, polysiloxanes, epoxides, polymers and copolymers of acrylonitrile and acrylates, and rubbers.

TABLE 2.4 Commercial Blowing (Foaming) Agents

Chemical Type	Decomposition Temperature in Air (°C)	Decomposition Position Range in Plastics (°C)	Gas Yield (mL/g)
<i>Azo compounds</i>			
Azobisformamide (Azodicarbonamide) (ABFA)	195–200	160–200	220
Azobisisobutyronitrile (AIBN)	115	90–115	130
Diazoaminobenzene (DAB)	103	95–100	115
<i>N-Nitroso compounds</i>			
N, N′-Dimethyl-N, N′-dinitrosoterephthalimide (DMTA)	105	90–105	126
N, N′-Dinitrosopentamethylenetetramine (DNPA)	195	130–190	265
<i>Sulfonyl hydrazides</i>			
Benzenesulfonylhydrazide (BSH)	> 95	95–100	130
Toluene-(4)-sulfonyl hydrazide (TSH)	103	100–106	120
Benzene-1, 3-disulfonyl hydrazide (BDH)	146	115–130	85
4, 4′-oxybis(benzenesulfonylhydrazide) (OBSH)	150	120–140	125

Source: Lasman, H. R. 1967. *Mod Plastics*, 45, 1A, Encycl. Issue, 368.

Diazoaminobenzene (DAB) is one of the first organic blowing agents to find industrial application. Its decomposition point (95°C–150°C) and gas number (115 cm³/g) depend on the pH of the medium; in acidic media it decomposes at lower temperature and more completely. DAB is used in foaming phenolic and epoxy resins, PVC, rubber and other high polymers.

N,N'-Dinitrosopentamethylenetetramine (DNPA) is the cheapest (except for urea oxalate) and most widely used organic blowing agent accounting for 50% of all blowing agents used. It however disperses poorly in mixtures and is sensitive to shock and friction (explosive).

Because of the relatively low temperature of decomposition, DTA can be used to make foams with a uniform cellular structure without deterioration of the polymer. The disadvantages of DTA are, however, poor dispersive ability in mixtures and sensitivity to moisture. Nevertheless, DTA is used in foaming PVC (especially for thin walled articles), polyurethane, polystyrene, polyamides, and siloxane rubbers.

BSH is used for foaming rubbers, polystyrene, epoxy resins, polyamides, PVC, polyesters, phenol-formaldehyde resins, and polyolefins. However, the thermal decomposition of BSH yields not only nitrogen but also a nontoxic residue (disulfide and thiosulfone) which may degrade to give thiophenol and thus an unpleasant odor to the foams.

OBSH is one of the best blowing agents of the sulfonylhydrazide class. Its gas liberation characteristics (no stepwise change up to 140°C) makes it possible to obtain foams with small, uniform cells. It is nontoxic and does not impart color and smell to articles. OBSH is used for foaming PVC, polyolefins, polysulfides, microporous rubber, or foamed materials based on mixtures of polymers with rubbers. In the last case, OBSH acts additionally as a cross-linking agent.

Closed-cell foams result when the decomposition and gelation are carried out in a closed mold almost filled with plastisol. After the heating cycle, the material is cooled in the mold under pressure until it is dimensionally stable. The mold is then opened, and the free article is again subjected to heat (below the previous molding temperature) for final expansion. Protective padding, life jackets, buoys, and floats are some items made by this process.

The blowing agents given in Table 2.4 can be used to make foamed rubber. A stable network in this product results from the cross-linking reaction (vulcanization), which thus corresponds to the step of fusion in the case of plastisols. Some thermoplastics also can be foamed by thermal decomposition of blowing agents even though they do not undergo an increase in dimensional stability at an elevated temperature. In this case the viscosity of the melt is high enough to slow down the collapse of gas bubbles so that when the polymer is cooled below its T_m a reasonably uniform cell structure can be built in. Cellular polyethylene is made in this way.

2.17.11 Special Foams

Some special types of foams are: (1) structural foams; (2) syntactic foams and multifoams; and (3) reinforced foams. Structural foams (Figure 2.58c and d), which possess full-density skins and cellular cores, are similar to structural sandwich constructions or to human bones, which have solid surfaces but cellular cores. Structural foams may be manufactured by high pressure processes or by low-pressure processes (Figure 2.61). The first one may provide denser, smoother skins with greater fidelity to fine detail in the mold than may be true of low-pressure processes. Fine wood detail, for example, is used for simulated wood furniture and simulated wood beams. Surfaces made by low-pressure processes may, however, show swirl or other textures, not necessarily detracting from their usefulness. Almost any thermoplastic or thermosetting polymer can be formulated into a structural foam.

In the case of syntactic foams (or spheroplastics), instead of employing a blowing agent to form bubbles in the polymer mass, hollow spherical particles, called microspheres, microcapsules, or microballoons, are embedded in a matrix of unblown polymer. (In *multifoams*, microspheres are combined with a foamed polymer to provide both kinds of cells.) Since the polymer matrix is not foamed, but is filled mechanically with the hollow spheres, syntactic materials may also be thought of as

reinforced or filled plastics, with the gas-containing particles being the reinforcing component. Synthetic wood, for instance, is provided by a mixture of polyester and small hollow glass spheres (microspheres).

The cellular structure of the syntactic foam depends on the size, quantity, and distributive uniformity of the microspheres. Since the microspheres have continuous shells, the final material will, as a rule, have completely enclosed cells, and thus can be called absolute foamed plastics or “absolute” closed-cell foams. This, together with the absence of microstructural anisotropy (because the microspheres have practically all the same size and are uniformly distributed in the matrix), gives a syntactic material its valuable properties. They have better strength-to-weight ratios than conventional foamed plastics, absorb less water, and can withstand considerable hydrostatic pressures. Using hollow sphere means that the final material is lighter than one containing a compact filler, such as glass powder, talc, kaolin, quartz meal, or asbestos.

Figure 2.70a and b are graphical presentations of syntactic foam structure in which the two components, microspheres and resin fill completely the whole volume (no dispersed voids) and the density of the product is thus calculated from the relative proportion of the two. Measured density values often differ from the calculated ones due to the existence of some isolated or interconnected irregularly shaped voids, as shown in Figure 2.70c. The voids are usually an incidental part of the composite, as it is not easy to avoid their formation. Nevertheless, voids are often introduced intentionally to reduce the density below the minimum possible in a close-packed two-phase structure (Figure 2.70a).

Syntactic foams exhibit their best mechanical behavior in the compressive mode. The spheres themselves are an extremely strong structure and hence can withstand such stresses very well. Syntactic materials consisting of hollow glass microspheres in epoxy resin are used for sandwich structures and as potting compounds for high-density electronic modules and other units likely to encounter hydrostatic pressures. Hollow glass microspheres and powdered aluminum in resin are used as core materials for sandwich construction and radomes. Hollow glass microspheres in aluminum matrix are used for aerospace and extreme hydrostatic pressure (oceanographic) applications in view of low weight and high compressive strength.

Polymer foams may be reinforced, usually with short glass fibers, and also other fibers such as asbestos or metal, and other reinforcements such as carbon black. The reinforcing agent is generally introduced into the basic components and is blown along with them, to form part of and to reinforce the walls of the cells (Figure 2.58e). When this is done, it is not unusual to obtain increases in mechanical properties of 400–500% with fiberglass content up to 50% by weight, especially in thermosettings. The principal advantages of reinforcement, in addition to increased strength and stiffness, are improved dimensional stability, resistance to extremes of temperature and resistance to creep.

Two processes for the manufacture of glass-reinforced foam laminates used as building materials, namely, free-rise process and restrained rise process are presented in Figure 2.71 and Figure 2.72. The glass fiber reinforcement is a thin (0.25–1.25 mm) mat supplied in roll form. It consists of layers of relatively long (1.5–4 m) glass fibers, the fibers in one layer being at an acute angle to the fibers in each next adjacent layer. A small amount of silane-modified polyester, or other binder is present, at a level of 2%–10% by weight. This type of glass mat is relatively porous to the passage of liquids and is also capable of expanding within a mixture of rising foam chemicals to provide a uniform, three-dimensional

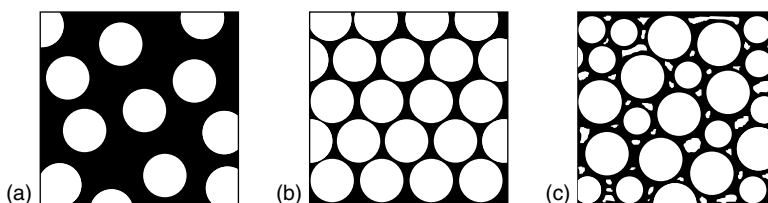


FIGURE 2.70 Graphical representations of syntactic foam structures. (a) Two-phase composite with random dispersion of spheres. (b) Two-phase composite with hexagonal close-packed structure of uniform sized spheres (74% by vol.). (c) Three-phase composite containing packed microspheres, dispersed voids and binding resin.

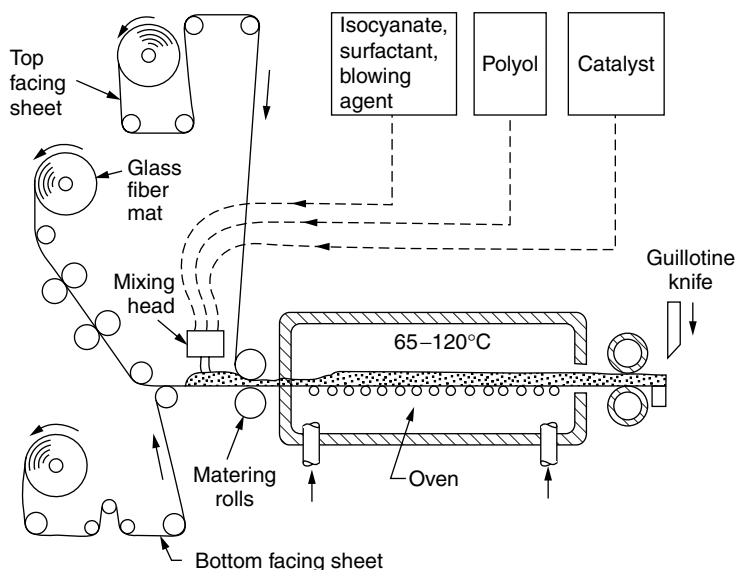


FIGURE 2.71 Schematic of a free-rise process for manufacture of glass-reinforced foam laminates.

reinforcing network within the final foamed laminate. The glass fiber reinforcement is functionally effective when used at levels of 4–24 g per board foot of the laminate [40]. Various types of facing sheets may be used, such as aluminum foil for building insulation products, asphalt-saturated felts for roof insulation or any other material, e.g., paper and plastic films.

2.18 Rubber Compounding and Processing Technology

2.18.1 Compounding Ingredients

No rubber becomes technically useful if its molecules are not cross-linked, at least partially, by a process known as curing or vulcanization [41–44]. For NR and many synthetic rubbers, particularly the diene rubbers, the curing agent most commonly used is sulfur. But sulfur curing takes place at technically viable rates only at a relatively high temperature ($>140^{\circ}\text{C}$) and, moreover, if sulfur alone is used, optimum curing requires use of a fairly high dose of sulfur, typically 8–10 parts per hundred parts of rubber (phr), and heating for nearly 8 h at 140°C .

Sulfur dose has been substantially lowered, however, with the advent of organic accelerators. Thus, incorporation of only 0.2–2.0 phr of accelerator allows reduction of sulfur dose from 8–10 to 0.5–3 phr and effective curing is achieved in a time scale of a few minutes to nearly an hour depending on temperature (100°C – 140°C) and type of the selected accelerator. The low sulfur dose required in the accelerated sulfur vulcanization has not only eliminated bloom (migration of unreacted sulfur to the surface of the vulcanizate), which was a common feature of the earlier nonaccelerated technology, but also has led to the production of vulcanizates of greatly improved physical properties and good resistance to heat and aging.

The selection of the accelerator depends largely on the nature of the rubber taken, the design of the product, and the processing conditions. It is important to adopt a vulcanizing system that not only gives a rapid and effective cross-linking at the desired vulcanizing temperatures but also resists premature vulcanization (scorching) at somewhat lower temperatures encountered in such operations as mixing, extrusion, calendaring, and otherwise shaping the rubber before final cross-linking. This may require the use of delayed-action type accelerators as exemplified by sulfenamides. Other principal types of accelerators with different properties are guanidines, thiazoles, dithiocarbamates, thiurams, and

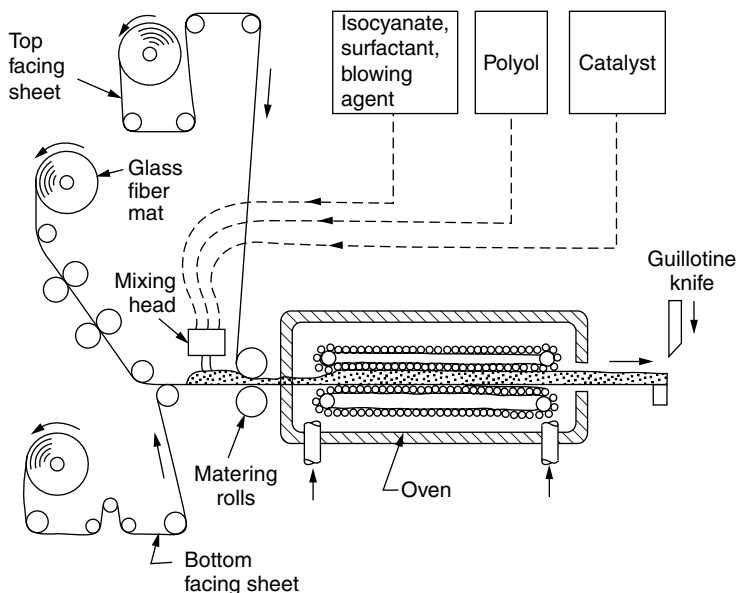


FIGURE 2.72 Schematic of a restrained rise process for manufacture of glass-reinforced foam laminates.

xanthates (Table 2.5). Accelerators are more appropriately classified according to the speed of curing induced in their presence in NR systems. In the order of increasing speed of curing, they are classified as slow, medium, semimultra, and ultra accelerators.

The problem of scorching or premature vulcanization is very acute with ultra or fast accelerators. Rubber stocks are usually bad conductors of heat and therefore flow of heat to the interior of a vulcanizing stock from outside is very slow. As a result, in thick items the outer layers may reach a state of overcuring before the core or interior layers begin to cure. For such thick items, a slow accelerator (Table 2.5) is most suitable.

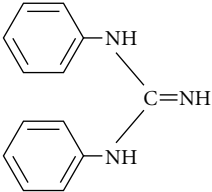
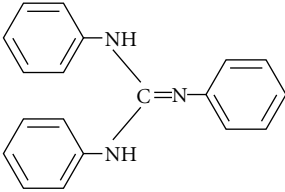
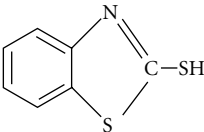
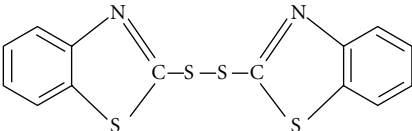
For butyl and EPDM rubbers, which have very limited unsaturations, slow accelerators are, however, unsuitable and, fast accelerators should be used at high temperatures for good curing at convenient rates. Since butyl rubber is characterized by reversion a phenomenon of decrease of tensile strength and modulus with time of cure after reaching a maximum, duration of heating at curing temperatures must be carefully controlled, and prolonged heating must be avoided.

For rubbers with higher degree of unsaturations, an ideal accelerator is one that is stable during mixing, processing, and storage of the mix, but that reacts and decomposes sharply at the high vulcanization temperature to effect fast curing. These requirements or demands are closely fulfilled by the delayed-action accelerators typical examples of which are given in Table 2.5.

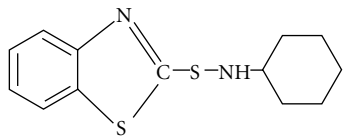
The spectacular effects of modern organic accelerators in sulfur vulcanization of rubber are observed only in the presence of some other additives known as accelerator activators. They are usually two-component systems comprising a metal oxide and a fatty acid. The primary requirement for satisfactory activation of accelerator is good dispersibility or solubility of the activators in rubber. Oxides of bivalent metals such as zinc, calcium, magnesium, lead, and cadmium act as activators in combination with stearic acid. A combination of zinc oxide and stearic acid is almost universally used. (Where a high degree of transparency is required, the activator may be a fatty acid salt such as zinc stearate.) Besides speeding up the rate of curing, activators also bring about improvements in physical properties of vulcanizates. This is highlighted by the data given in Table 2.6.

A sulfur-curing system thus has basically four components: a sulfur vulcanizing agent, an accelerator (sometimes combinations of accelerators), a metal oxide, and a fatty acid. In addition, in order to improve

TABLE 2.5 Accelerator for Sulfur Vulcanization of Rubbers

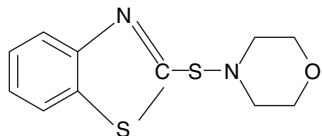
Accelerator Type and Formula	Chemical Name	Accelerator Activity
Guanidines		
	Diphenyl guanidine (DPG)	Medium accelerator
	Triphenyl guanidine (TPG)	Slow accelerator
Thiazoles		
	Mercaptobenzothiazole (MBT)	Semi-ultra accelerator
	Mercaptobenzothiazyl disulfide (MBTS) ^a	Semi-ultra (delayed action) accelerator

Sulfenamides



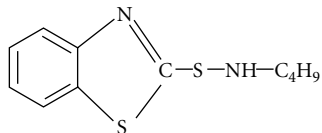
N-Cyclohexyl benzothiazyl sulfenamide (CBS)

Semi-ultra (delayed action) accelerator



N-Oxydiethylenebenzothiazyl sulfenamide (NOBS) or 2-Morpholinothiobenzothiazole (MBS)

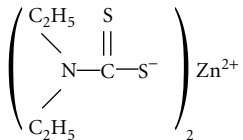
Semi-ultra (delayed action) accelerator



N-t-Butylbenzothiazyl sulfenamide (TBBS)

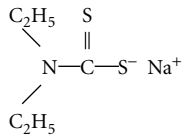
Semi-ultra (delayed action) accelerator

Dithiocarbamates



Zinc diethyl Dithiocarbamate (ZDC)

Ultra accelerator



Sodium diethyl dithiocarbamate (SDC)

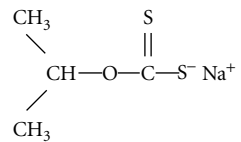
Ultra accelerator, water soluble (used for latex)

(continued)

Table 2.5 (Continued)

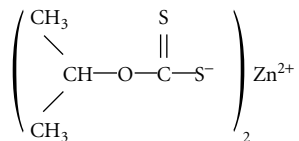
Accelerator Type and Formula	Chemical Name	Accelerator Activity
Thiuram sulfides		
<p>The structure shows two nitrogen atoms connected by a disulfide bridge (-S-S-). Each nitrogen is double-bonded to a carbon atom, which is in turn single-bonded to two methyl groups (CH₃).</p>	Tetramethyl thiuram disulfide (TMTD, TMT) ^a	Ultra accelerator
<p>The structure is similar to TMTD, but the methyl groups are replaced by ethyl groups (C₂H₅).</p>	Tetraethyl thiuram disulfide (TETD, TET) ^a	Ultra accelerator
<p>The structure shows two nitrogen atoms connected by a monosulfide bridge (-S-). Each nitrogen is double-bonded to a carbon atom, which is in turn single-bonded to two methyl groups (CH₃).</p>	Tetramethyl thiuram monosulfide (TMTM)	Ultra accelerator

Xanthates



Sodium isopropyl xanthate (SIX)

Ultra accelerator, water soluble
(suited for latex)



Zinc isopropyl xanthate (ZIX)

Ultra accelerator

^a Sulfur donors.

TABLE 2.6 Effect of Activator on Vulcanization

Time of Cure (min)	Tensile Strength, Psi (MPa)	
	ZnO (phr)	
	0.0	5.0
	100 (0.7)	2300 (16)
30	400 (2.8)	2900 (20)
60	1050 (7.2)	2900 (20)
90	1300 (9.0)	2900 (20)

Base compound: NR (pale creep) 100; sulfur 3; mercaptobenzothiazole (MBT) 0.5. Temperature of vulcanization 142°C.

the resistance to scorching, a prevulcanization inhibitor such as *N*-cyclohexylthiophthalimide may be incorporated without adverse effects on either the rate of cure or physical properties of the vulcanizate.

The level of accelerator used varies from polymer to polymer. Some typical curing systems for the diene rubbers (NR, SBR, and NBR) and for two olefin rubbers (IIR and EPDM—see [Appendix A2](#) for abbreviations) are given in Table 2.7.

In addition to the components of the vulcanization system, several other additives are commonly used with diene rubbers. Rubbers in general, and diene rubbers in particular, are blended with many more additives than is common for most thermoplastics with the possible exceptions of PVC. The major additional classes of additives are:

1. Antidegradants (antioxidants and antiozonants)
2. Processing aids (peptizers, plasticizers, softeners, and extenders, tackifiers, etc.)
3. Fillers
4. Pigments
5. Others (retarders, blowing agents)

The use of antioxidants and antiozonants has already been described in [Chapter 1](#).

2.18.1.1 Processing Aids

Peptizers are added to rubber at the beginning of mastication (see later) and are used to increase the efficiency of mastication. They act chemically and effectively at temperatures greater than 65°C and hasten the rate of breakdown of rubber chains during mastication. Common peptizers are zinc thiobenzoate, zinc-2-benzamidothiophenate, thio- β -naphthol, etc. Processing aids other than the peptizer and compounding ingredients (additives) are added after the rubber attains the desired plasticity on mastication.

Common process aids, besides the peptizer, are pine tar, mineral oil, wax, factice, coumarone-indene resins, petroleum resins, rosin derivatives, and polyterpenes. Their main effect is to make rubber soft and

TABLE 2.7 Components of Sulfur Vulcanization Systems

Additive ^a (phr)	Rubber				
	NR	SBR	NBR	IIR	EPDM
Sulfur	2.5	2.0	1.5	2.0	1.5
Zinc oxide	5.0	5.0	5.0	3.0	5.0
Stearic acid	2.0	2.0	1.0	2.0	1.0
TBBS	0.6	1.0	—	—	—
MBTS	—	—	1.0	0.5	—
MBT	—	—	—	—	1.5
TMTD	—	—	0.1	1.0	0.5

^a See [Table 2.5](#) for accelerator abbreviations.

tacky to facilitate uniform mixing, particularly when high loading of carbon black or other fillers is to be used.

Factice (vulcanized oil) is a soft material made by treating drying or semidrying vegetable oils with sulfur monochloride (cold or white factice) or by heating the oils with sulfur at 140–160°C (hot or brown factice). The use of factice (5–30 phr) allows efficient mixing and dispersion of powdery ingredients and gives a better rubber mix for the purpose of extrusion.

Ester plasticizers (phthalates and phosphates) that are used to plasticize PVC (see [Chapter 1](#)) are also used as process aids, particularly with NBR and CR. Polymerizable plasticizers such as ethylene glycol dimethacrylate are particularly useful for peroxide curing rubbers. They act as plasticizers or tackifiers during mixing and undergo polymerization by peroxide initiation during cure.

The diene hydrocarbon rubbers are often blended with hydrocarbon oils. The oils decrease polymer viscosity and reduce hardness and low temperatures brittle point of the cured product. They are thus closely analogous to the plasticizers used with thermoplastics but are generally known as softeners. Three main types of softeners are distinguished: aliphatic, aromatic, and naphthenic. The naphthenics are preferred for general all-round properties.

NRs exhibit the phenomenon known as tack. Thus when two clean surfaces of masticated rubber are brought into contact the two surfaces strongly adhere to each other, which is a consequence of interpenetration of molecular ends followed by crystallization. Amorphous rubbers such as SBR do not display such tack and it is necessary to add tackifiers such as rosin derivatives and polyterpenes.

2.18.1.2 Fillers

The principles of use of inert fillers, pigments, and blowing agents generally follow those described in Chapter 1. Major fillers used in the rubber industry are classified as (1) nonblack fillers such as china clay, whiting, magnesium carbonate, hydrated alumina, anhydrous, and hydrated silicas and silicates including those in the form of ground mineral such as slate powder, talc, or French chalk, and (2) carbon blacks.

Rather peculiar to the rubber industry is the use of the fine particle size reinforcing fillers, particularly carbon black. Fillers may be used from 50 phr to as high as 100–120 phr or even higher proportions. Their use improves such properties as modulus, tear strength, abrasion resistance, and hardness. They are essential with amorphous rubbers such as SBR and polybutadiene that has little strength without them. They are less essential with strain-crystallizing rubbers such as NR for many applications but are important in the manufacture of tires and related products.

Carbon blacks are essentially elemental carbon and are produced by thermal decomposition or partial combustion of liquid or gaseous hydrocarbons to carbon and hydrogen. The principal types, according to their method of production, are channel black, furnace black, and thermal black.

Thermal black is made from natural gas by the thermatomic process in which methane is cracked over hot bricks at a temperature of 1,600°F (871°C) to form amorphous carbon and hydrogen. Thermal black consists of relatively coarse particles and is used principally as a pigment. A few grades (FT and MT referring to fine thermal and medium thermal) are also used in the rubber industry.

Most of the carbon black used in the rubber industry is made by the furnace process (furnace black), that is, by burning natural gas or vaporized aromatic hydrocarbon oil in a closed furnace with about 50% of the air required for complete combustion. Furnace black produced from natural gas has an intermediate particle size, while that produced from oil can be made in wide range of controlled particle sizes and is particularly suitable for reinforcing rubbers.

Quite a variety of grades of furnace blacks are available, e.g., fine furnace black (FF), high modulus (HMF), high elongation (HEF), reinforcing (RF), semireinforcing (SRF), high abrasion (HAF), super abrasion (SAF), intermediate super abrasion (ISAF), fast extruding (FEF), general purpose (GPF), easy processing (EPF), conducting (CF), and super conducting furnace black (SCF).

Channel black is characterized by lower pH, higher volatile content, and high surface area. It has the smallest particle size of any industrial material. A few grades of channel blacks (HPC, MPC, or EPC corresponding to hard, medium, or easy processing channel) are used in the rubber industry.

For carbon-black fillers, structure, particle size, particle porosity, and overall physico-chemical nature of particle surface are important factors in deciding cure rate and degree of reinforcement attainable. The pH of the carbon black has a profound influence. Acidic blacks (channel blacks) tend to retard the curing process while alkaline blacks (furnace blacks) produce a rate-enhancing effect in relation to curing, and may even give rise to scorching.

Another important factor is the particle size of the carbon black filler. The smaller the particle size, the higher the reinforcement, but the poorer the processability because of the longer time needed for dispersion and the greater heat produced during mixing. Blacks of the smallest particle size are thus unsuitable for use in rubber compounding.

For carbon black fillers the term *structure* is used to represent the clustering together and entanglement of fine carbon particles into long chains and three-dimensional aggregates. High-structure blacks produce high-modulus vulcanizates as high shear forces applied during mixing break the agglomerates down to many active free radical sites, which bind the rubber molecules, thereby leading to greater reinforcement. In nonstructure blacks the aggregates are almost nonexistent.

Most of the nonblack fillers used in rubber compounds are of nonreinforcing types. They are added for various objectives, the most important being cost reduction. Precipitated silica (hydrated), containing about 10–12% water with average particle size ranging 10–40 nm, produce effective reinforcements and are widely used in translucent and colored products. Finely ground magnesium carbonate and aluminum silicate also induce good reinforcing effects. Precipitated calcium carbonate and activated calcium carbonate (obtained by treating calcium carbonate with a stearate) are used as semireinforcing fillers.

Short fibers of cotton, rayon, or nylon may be added to rubber to enhance modulus and tear and abrasion resistance of the vulcanizates. Some resins such as “high styrene resins” and novolac-type phenolic resins mixed with hexamethylene tetramine may also be used as reinforcing fillers or additives. Whereas SBR has a styrene content of about 23.5% and is rubbery, styrene-butadiene copolymers containing about 50% styrene are leatherlike whilst with 70% styrene the materials are more rigid thermo-plastics but with low softening points. Both of these copolymers are known in the rubber industry as high styrene resins and are usually blended with a hydrocarbon rubber such as NR and SBR. Such blends have found use in shoe soles, car wash brushes and other moldings, but in recent years have suffered increasing competition from conventional thermoplastics and thermoplastic rubbers.

2.18.2 Mastication and Mixing

A deficiency of NR, compared with the synthetics, is its very high molecular weight, which makes mixing of compounding ingredients and subsequent processing by extrusion and other shaping operations difficult. For NR it is thus absolutely necessary, while for synthetic rubbers it is helpful, to subject the stock to a process of breakdown of the molecular chains prior to compounding. This is effected by subjecting the rubber to high mechanical work (shearing action), a process commonly known as *mastication*. Mastication and mixing are conveniently done using two-roll mills and internal mixers. The oxygen in air plays a critical role during mastication.

Rubber that has been masticated is more soft and flows more readily than the unmasticated material also allows preparation of solutions of high solids content because of the much lower solution viscosity of the degraded rubber. Rubber is also rendered tacky by mastication, which means that the uncured rubber sticks to itself readily so that articles of suitable thickness can be built up from layers of masticated rubber or rubberized fabric without the use of a solvent.

2.18.2.1 Open Mill

The mainstays of the rubber industry for over 70 years has been the two-roll (open) mill and the Banbury (internal) mixer. Roll mills were first used for rubber mixing over 120 years ago. The plastics and adhesives industries later adopted these tools.

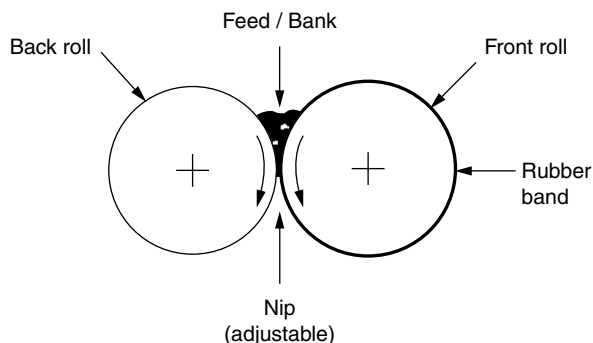


FIGURE 2.73 Section showing the features of a two-roll open mill.

The two-roll mill (Figure 2.73) consists of two opposite-rotating rollers placed close to one another with the roll axes parallel and horizontal, so that relatively small gap or nip (adjustable) between the cylindrical surface exists. The speeds of the two rolls are usually different, the front roll having a slower speeds. For NR mixing, a friction ratio of 1:1.2 for the front to back roll may be used. For some synthetic rubbers or highly filled NR mixes, friction ratios close to 1.0 produce good results.

The nip is adjusted so that when pieces of rubber are placed between the rolls, they are deformed by shearing action and squeezed through the nip to which they are returned by the operator. On repeated passage through the nip, the around the front roll and a moving “bank” above the nip. As the rolls keep on rotating, the operator uses a knife to cut through the band on the front roll, removes the mass in parts from time, and places it a new position to ensure uniform treatment and mixing through the nip.

With most rubbers other than NR, addition of different compounding ingredients may be normally started soon after a uniform band is formed on the roll and a bank is obtained. For NR, however, milling is usually continued to masticate the rubber to the desired plasticity, and mixing of compounding ingredients is started only after the adequate mastication. Mixing is effected by adding the different ingredients onto the bank. They are gradually dispersed into the rubber, which is cut at intervals, rolled over, and recycled through the nip of the moving rolls to produce uniform mixing.

Since the rate of mastication is a function of temperature, time and temperature of mastication have to be controlled or kept uniform from batch to batch in order to get the desired uniform products from different batches.

Roll mills vary greatly in size from very small laboratory machines with rollers of about 1 in. in diameter and driven by fractional horsepower motors to very large mills with rollers of nearly 3 ft. in diameter and 7 or 8 ft. in length and driven by motors over 100 hp.

2.18.2.2 Internal Batch Mixers

Internal batch mixers are widely used in the rubber industry. They are also used for processing plastics such as vinyl, polyolefins, ABS, and polystyrene, along with thermosets such melamines and ureas because they can hold materials at a constant temperature.

The principle of internal batch mixing was first introduced in 1916 with the development of the Banbury mixer (Figure 2.74a). A Banbury-type internal mixer essentially consists of a cylindrical chamber or shall within which materials to be mixed are deformed by rotating blades or rotors with protrusions. The mixer is provided with a feed door and hopper at the top and a discharge door at the bottom. As the rubber or mix is worked and sheared between the two rotors and between each rotor and the body of the casing, mastication takes place over the wide area, unlike in a open mill where it is restricted only in the area of the nip between the two rolls.

The rotor blade of the Banbury mixer is pear shaped, but the projection is spiral along the axis and the two spirals interlock and rotate in opposite directions (Figure 2.74b). The interaction of rotor blades between themselves, in addition to producing shearing action, causes folding or “shuffling” of the mass,

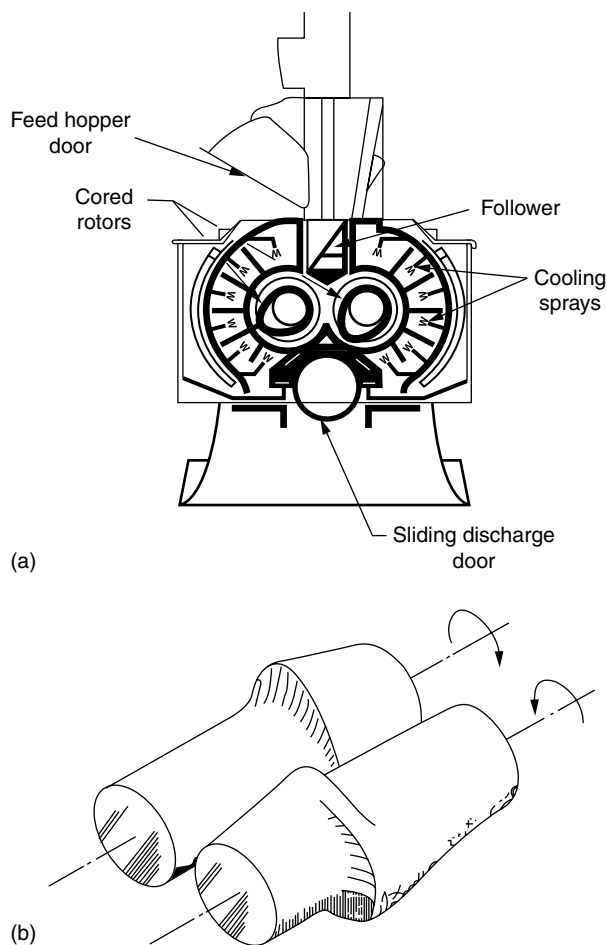


FIGURE 2.74 (a) Cross-section of a Banbury mixer; (b) Roll mixing blades in Banbury mixer.

which is further accentuated by the helical arrangement of the blade along the axis of the rotor, thereby imparting motion to the mass in the third, or axial, direction. This combination of intensive working produces a highly homogeneous mix.

An important and novel feature of the Banbury mixer is a vertical ram to press the mass into contact with the two rotors. Rubbers, fillers, and other ingredients are charged through the feed hopper and then held in the mixing chamber under the pressure of the hydraulic (or manual) ram. As a result, incorporation of solids is more rapid. Both the cored rotors and the walls of the mixing chamber can be cooled or heated by circulating fluid. Because of the large power consumption of such a machine (up to 500 hp) the cylinder walls are usually water-cooled by sprays (Figure 2.74a).

Other major machines in use in the rubber industry are the Shaw intermix and the Baker-Perkins shear-mix. Both the Banbury-type and the intermix mixers have passed through modifications and refinements at different points in time. Mechanical feeding and direct oil injection in measured doses into the mixing chamber through a separate oil injection port are notable features of modern internal mixers. Higher rotor speeds and, in the Banbury type, the higher ram pressures, are used for speedy output.

In Banbury-type mixers, the rotors run at different speeds, while in intermix mixers the rotor speeds are equal but the kneading action between the thicker portion of one rotor and the thinner portion of the other produces a frictional effect.

The operation of internal mixers is power intensive, and a given job is performed at a much higher speed and in a much shorter time on a two-roll open mill. However, the major vulcanizing agent (such as sulfur) is often added later on a two-roll mill so as to eliminate possibilities of scorching. And even if this is not practiced, the mix, after being discharged from the internal mixer, is usually passed through a two-roll mill in order to convert it from irregular lumps to a sheet form for convenience in subsequent processing.

2.18.3 Reclaimed Rubber

The use of reclaimed rubber in a fresh rubber mix not only amounts to waste utilization but offers some processing and economic advantages to make it highly valued in rubber compounding. Though waste vulcanized rubber is normally not processable, application of heat and chemical agents to ground vulcanized waste rubber leads to substantial depolymerization whereby conversion of the rubber to a soft, plastic processable state is effected. Rubber so regenerated for reuse is commonly known as reclaimed rubber or simply as reclaim. Reclaimed rubber can be easily revulcanized.

Worn-out tires and scraps and trimmings of other vulcanized products constitute the raw material for reclaimed rubber. Therefore a good reclaiming process must not only turn the rubber soft and plastic but also must remove reinforcing cords and fabrics that may be present. There are a number of commercial processes [43] for rubber regeneration: (1) alkali digestion process, (2) neutral or zinc chloride digestion process, (3) heater or pan process, and (4) reclaimator process.

Tires are most commonly reclaimed by digestion processes. For processes (1) and (2), debaded tires and scraps, cut into pieces, are ground with two-roll mills or other devices developed for the purpose. Two-roll mills generally used for grinding tires turn at a ratio of about 1:3, thus providing the shearing action necessary to rip the tire apart. The rubber chunks are screened, and the larger material is recycled until the desired size is reached. The ground rubber is then mixed with a peptizer, softener, and heavy naphtha, and charged into spherical autoclaves with requisite quantities of water containing caustic soda for process (1) or zinc chloride for process (2).

The textile is destroyed and mostly lost in the digestion process. Steam pressure and also the amount of air or oxygen in the autoclave greatly influence the period necessary for rubber reclaiming. On completion of the process, the pressure is released, the contents of the autoclave discharged into water, centrifuged, pressed to squeeze out water, and dried. The material is finally processed through a two-roll mill during which mineral fillers and oils may be added to give a product of required specific gravity and oil extension.

Butyl and NR tubes and other fiber-free scrap rubbers are reclaimed by means of the heater or pan process. Brass tube fittings and other metal are removed from the scrap. The scrap is mechanically ground, mixed with reclaiming agents, loaded into pans or devulcanizing boats, and autoclaved at steam pressures of 10–14 atm (1.03–1.40 MPa) for 3–8 h. The reclaim is finally processed much the same way as in the digester process.

The reclaimator process is more attractive than the above processes. The reclaimator is essentially a high-pressure extruder that devulcanizes fiber-free rubber continuously. Ground scrap is mechanically treated in hammer mills to remove the textile material, mixed with reclaiming oils and other materials, and then fed into the reclaimator. High pressure and shear between the rubber mixture and the extruder barrel walls effectively reclaim the rubber mixture. Devulcanization occurs at 175–205°C in a few minutes and turns the rubber into reclaim that issues from the machine continuously. The whole regeneration, which is a dry process, may be completed in about 30 min.

The reclaiming oils and chemicals are complex wood and petroleum derivatives that swell the rubber and provide access for breaking the rubber bonds with heat, pressure, chemicals, and mechanical shearing. Approximately 2–4 parts of oil are used per 100 parts of scrap rubber. Some examples of reclaiming oils include monocyclic and mixed terpenes, i.e., pine-tar products, saturated polymerized petroleum hydrocarbons, aryl disulfides in petroleum oil, cycloparafinic hydrocarbons, and alkyl aryl polyether alcohols.

Reclaimed rubber contains all the fillers present in the original scrap or waste rubber. It shows very good aging characteristics and is characterized by less heat development during mixing and processing as compared to fresh rubber. The use of reclaim in a fresh rubber mix is advantageous not on consideration of physical and mechanical properties but essentially for smooth processing and reduced cost.

Radial tires (see later) do not use reclaimed rubber because they require higher abrasion resistance that cannot be attained by mixing reclaimed rubber. Better processes for the production of higher quality reclaimed rubber are needed in order to use it for radial tires. To improve the quality of reclaimed rubber, cross-links in vulcanizates should be severed selectively during a devulcanization process and no low-molecular-weight compound such as swelling solvent should remain in the reclaimed rubber after the devulcanization process.

A devulcanization process that utilizes supercritical CO₂ as a devulcanization reaction medium in the presence of diphenyl disulfide as a devulcanizing reagent has been reported [45]. The process devulcanizes unfilled NR vulcanizates effectively. Further, a comparison of measured sol/gel components as well as dynamic mechanical properties of the devulcanized rubber products of filled and unfilled NR vulcanizates has indicated that the presence of carbon black in the vulcanizate does not disturb the devulcanization in supercritical CO₂.

2.18.4 Some Major Rubber Products

The most important application of rubbers is in the transport sector, with tires and related products consuming nearly 70% of the rubber produced. Next in importance is the application in belting for making flat conveyor and (power) transmission belts and V-belts (for power transmission), and in the hose industry for making different hoses. Rubber also has a large outlet in cellular and microcellular products. Other important and special applications of rubber are in the areas of adhesives, coated fabrics, rainwear, footwear, pipes and tubing, wire insulation, cables and sheaths, tank lining for chemical plants and oil storage, gaskets and diaphragms, rubber mats, rubber rollers, sports goods, toys and balloons, and a wide variety of molded mechanical and miscellaneous products. Formulations of a few selected rubber compounds are given in [Appendix A10](#).

2.18.4.1 Tires

Tire technology is a very specialized area, and a tire designer is faced with the difficult task of trying to satisfy all the needs of the vehicle manufacturer, the prime factors of consideration, however, being safety and tread life.

[Figure 2.75](#) shows the constructions of a standard bias (diagonal) ply tire and a radial ply tire. The major components of a tire are: bead, carcass, sidewall, and tread. In terms of material composition, a tire on an average contains nearly 50% of its weight in actual rubber; for oil extended rubbers (typically containing 25 parts of aromatic or cycloparaffinic oils to 75 parts of rubber), it is less. The remainder included carbon black, textile cord, and other compounding ingredients plus the beads.

The bead is constructed from a number of turns or coils of high tensile steel wire coated with copper and brass to ensure good adhesion of the rubber coating applied on it. The beads function as rigid, practically inextensible units that retain the inflated tire on the RIM.

The carcass forms the backbone of the tire. The main part of the carcass is the tire cord. The cords consist of textile threads twisted together. Rayon, nylon, and polyester cords are widely used. Steel cords are also used. While the practice of laying rubber-impregnated cords in position is still followed, the use of woven fabric is more widespread. To promote a good bond with rubber, the fiber or cord is treated with an adhesive composition such as water-soluble resorcinol-formaldehyde resin and aqueous emulsion of a copolymer of butadiene, styrene, and vinyl pyridine (70:15:15). The resincoated cord or fabric is dried and coated with a rubber compound by calendaring, whereby each cord is isolated from its neighbor. For conventional tires, the rubber-coated fabric is then cut to a predetermined width and bias angle. The bias-cut plies are joined end-to-end into a continuous length and batched into roll form, interleaved with a textile lining to prevent self-adhesion.

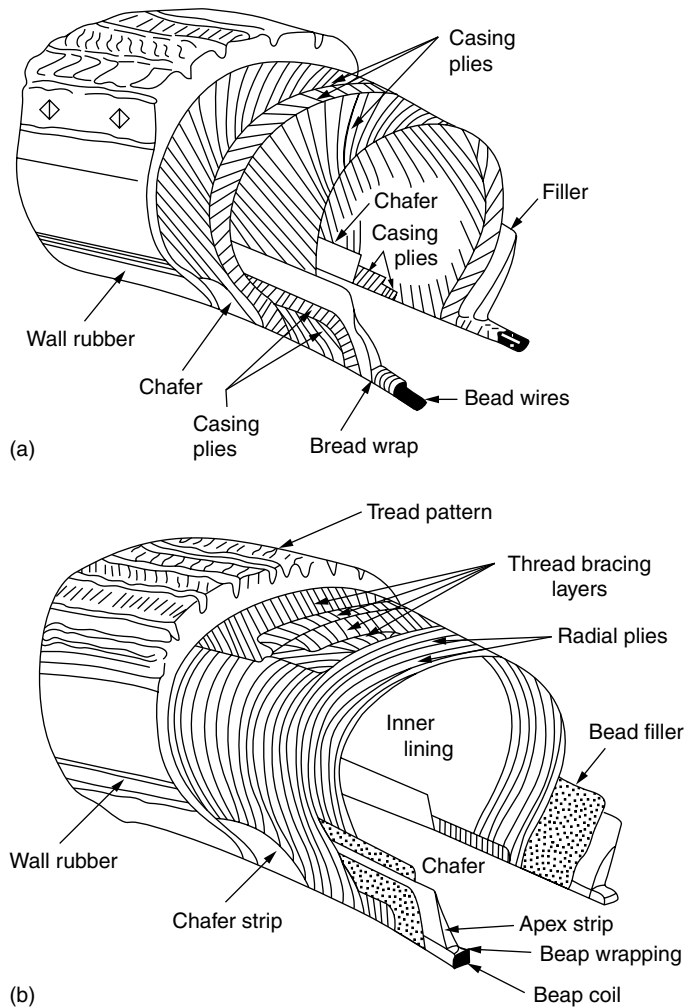


FIGURE 2.75 Diagram showing. (a) bias (diagonal) ply tire; and (b) radial ply tire.

The sidewall is a layer of extruded rubber compound that protects the carcass framework from weathering and from damage from chafing. Together with the tread and overlapping it in the buttress region, the sidewall forms the outermost layer of the tire. It is the most highly strained tire component and is susceptible to two types of failure—flex cracking and ozone cracking.

The tread is also formed by extrusion, but different rubber compounds are used for sidewall and tread (see [Appendix A10](#)). When making the side-wall and the tread in two separate extrusion lines, it is useful to take the extruded sidewall to the second extruder, which would deliver the tread to the sidewall. To simplify the tire-building operation, the sidewall and the tread may also be produced as a single unit by simultaneous extrusion of the two compounds in a single band—the tread over the sidewall—with two extruders arranged head-to-head with a common double die. The band is rapidly cooled to avoid scorching and then cut to the appropriate length. The tread receives its characteristic pattern from the mold when the subsequently built tire is vulcanized.

While building the tire, a layer of specially compounded cushion rubber may be used to keep heat development on flexing to a minimum and achieve better adhesion between the tread and the carcass.

One or more layers of fabric, known as breakers or bracing layers, may be placed below the cushion. The bracing layers raise the modulus of the tread zone and level out local blows to the tread as it contacts the road.

The tire building is carried out on a flat drum, which is rotated at a controlled speed. The plies of rubber-coated cord fabric are placed in position, one over the other, and rolled down as the drum rotates, the inner lining being placed next to the drum and the ends of the drum being flanged to suit the bead configuration of the tire. The plies of rubber-coated textile are assembled in three basic constructions—bias (diagonal), radial, and bias belted.

Bias tires have an even number of plies with cords at an angle of 30–38° from the tread center line. Passenger-car bias tires commonly have two or four plies, with six for heavy duty service. Truck tires are often built with six to twelve plies, although the larger earthmover types may contain thirty or more.

In the radial-ply tire, one or two plies are set at an angle of 90° from the center line and a *breaker* or *belt* or rubber-coated wire or textile is added under the tread. This construction gives a different tread-road interaction, resulting in a decreased rate of wear. The sidewall is thin and very flexible. The riding and steering qualities are noticeably different from those of a bias-ply tire and require different suspension systems.

The bias-belted tire, on the other hand, has much of the tread wear and traction advantage of the radial tire, but the shift from bias to bias-belted tires requires less radical change in vehicle suspension systems and in tire building machines. These features make the bias-belted tire attractive to both automobile and tire manufacturers.

When the tire building on the drum is complete, the drum is collapsed and the uncured (“green”) tire is removed. The cylindrical shape of the uncured tire obtained from the building drum is transformed into a toroidal shape in the mold resulting in a circumferential stretch of the order of 60%. For shaping and curing, the uncured tire is pressed against the inner face of the heated mold by an internal bag or bladder made of a pre-cured heat-resistant rubber and inflated by a high-pressure steam or circulating hot water. Different types of molding presses are in use. In the Bag-O-Matic type of press, the uncured tire is placed over a special type of bag or bladder, and the operation of shaping, curing, and ejection of the cured tire are accomplished by an automatic sequence of machine operation.

Pneumatic tires require an air container or inner tube of rubber inside the tire. The manufacture of inner tubes is done essentially in three steps: extrusion, cutting into length, and insertion of valve and vulcanization. The ends of the cut length of the tube are joined after insertion of the valve prior to vulcanization.

Tubeless tires have, instead of an inner tube, an *inner liner*, which is a layer of rubber cured inside the casing to contain the air, and a chafer around the bead contoured to form an airtight seal with the RIM.

2.18.4.2 Belting and Hoses

Uses of flat conveyor and (power) transmission belts and V-belts (for power transmission) are to be found in almost all major industries. V-belts for different types cover applications ranging from fan belts for automobiles, belts for low-power drives for domestic, laboratory, and light industrial applications, to high-power belts for large industrial applications.

Textile cords or fabric and even steel cords constitute an important part of all rubber belting and hoses. The various types of cords used in the tire industry are also in use in the belting industry.

Essential steps in making conveyor belts are: (1) drying the fabric; (2) frictioning of the hot fabric with a rubber compound and topping to give additional rubber between plies and the outer ply and cover, using a three- or four-roll calender; (3) belt building; and (4) vulcanization.

The process of belt building essentially consists of cutting, laying, and folding the frictioned and coated fabric to give the desired number of plies. The construction may be straight-laid or graded-ply types (Figure 2.76) with the joints in neighboring plies being staggered to eliminate weakness and failure. Finally, the cover coat is applied by calendaring.

Vulcanization of conveyor belts may be carried out in sections using press cure or continuously by means of a Rotocure equipment. In press cure, vulcanization is done by heating in long presses, the belt

being moved between successive cures by a length less than the length of the press platens. Since in this process the end or overlap zones receive an additional cure, it is desirable to minimize damage or weakness due to overcure by using flat cure mixes and allowing water cooling at each end section of the platen.

In each step of vulcanization, the section of the belt to be vulcanized is gripped and stretched hydraulically to minimize or eliminate elongation during use. The difficulties of press cure may, however, be avoided by adopting continuous vulcanization with a Rotocure equipment in which the actual curing operation is carried out between an internally steam heated cylinder and a heated steel band. Rotocure is also useful for the vulcanization of transmission belts and rubber sheeting.

The most common feature of V-belts is their having a cross-section of the shape of a regular trapezium with the unparallel sides at an angle of 40° (Figure 2.77). The V-belts usually consist of five sections: (1) the top section known as the tension section, (2) the bottom section, called the compression section, (3) the cord section located at the neutral zone, (4) the cushion section on either side of the cord section, and (5) one or two layers of rubberized fabric, called the jacket section covering the whole assembly.

Three different rubber compounds are required for use in the above construction of a V-belt: (1) a base compound, which is the major constituent on a weight basis, (2) a soft and resilient cushion compound required for surrounding and protecting the reinforcing cord assembly, and (3) a friction compound used for rubberizing the fabric casing of the belt (see [Appendix A10](#)).

Relatively short length V-belts are built layer by layer on rotatable collapsible drum formers. The separate belts are then cut out with knives and transferred to a skiving machine that imparts the desired V-shape. The fabric jacket is then applied, and the belts are vulcanized in open steam using multi-cavity ring molds for smaller belts. Long belts are built similarly on V-groove sheave pulleys using weftless cord fabric in place of individually wound cord. They are vulcanized endlessly by molding in a hydraulic press under controlled tension.

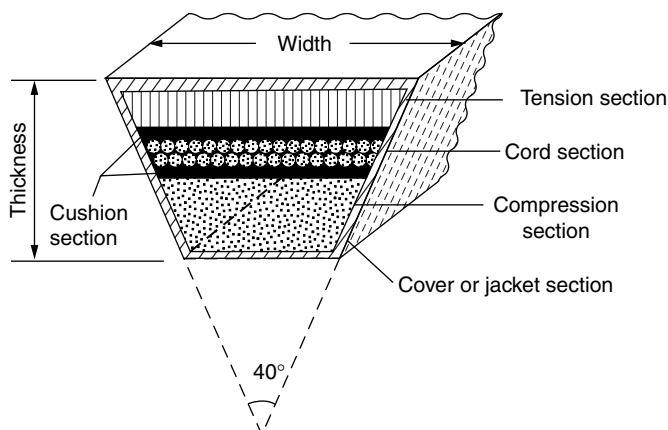


FIGURE 2.77 Cross-section showing V-belt construction.

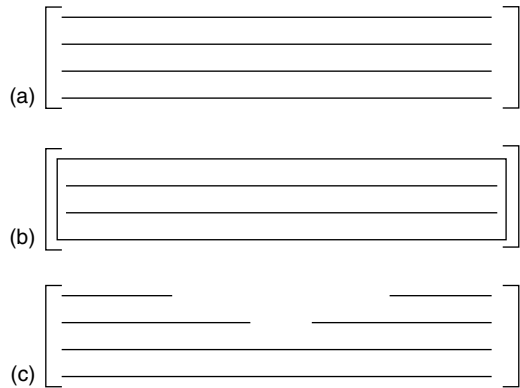


FIGURE 2.76 Construction of conveyor belts: (a) straight laid, (b) folded jacket, and (c) graded ply.

A rubber hose has three concentric layers along the length. While the innermost part consisting of a rubber lining or tube is required to resist the action of the material that would pass through the top layer is meant to play the role of a protective layer to resist weathering, oils, chemicals, abrasion, etc. Between the inner lining and the outer cover is given a layer of reinforcement of textile yarn or steel wire applied by spiraling, knitting, braiding, or circular loom weaving. A cut woven fabric wrapped straight or on the bias may also be used to reinforce the inner lining or tube.

Essentially, the process of hose building consists of extruding the lining or tube, braiding or spiraling the textile around the cooled tube, and applying an outer cover of rubber to the reinforced hose using a cross-head extruder. Several methods are employed for vulcanization. In one process, the built hose is passed through a lead press or lead extruder to give a layer of lead cover to the hose. The hose is then wound on a drum, filled with water or air, and the ends are sealed. The whole assembly is then heated to achieve vulcanization. The water or air inside expands, and the vulcanizing hose is pressed against the lead acting as the mold. On completion of cure, the sealed ends are cut open, the lead cover is removed by slitting lengthwise in a stripping machine, and the cured hose is coiled up.

2.18.4.3 Cellular Rubber Products

Cellular rubber may be described as an assembly of a multitude of cells distributed in a rubber matrix more or less uniformly. The cells may be interconnected (open cells) as in a sponge or separate (closed cells). Foam rubber made from a liquid starting material such as latex, described earlier, is of open-cell type. Cellular products made from solid rubber are commonly called sponge (open cell structure) and expanded rubber (closed cell structure).

The technology of making cellular products from solid rubber is solely dependent on the incorporation of a blowing agent, usually a gas such as nitrogen or a chemical blowing agent, into the rubber compound. The most widely used chemical blowing agent for this application is dinitroso pentamethylene tetramine (DNPT).

The curing is carried out either freely using hot or steam or in a mold that is only partially filled with the molding compound. Synthetic rubbers, particularly SBR, are preferred as they allow precise control over level of viscosity required for obtaining consistent product quality. The sponge and expanded rubber products include carpet backing, sheets, profiles, and molding.

The development of microcellular rubber has brought a revolution in footwear technology. Microcellular rubber with an extremely fine noncommunicating cell structure and very comfortable wearing properties, is the lightest form of soling that can be produced. Density of soling as low as 0.3 g/cm^3 may be obtained with a high dose (8–10 phr) of DNPT at a curing temperature of $140\text{--}150^\circ\text{C}$. For common solings, the density normally varies between 0.5 and 0.8 g/cm^3 .

High hardness and improved abrasion resistance along with low density, desired in microcellular soling, can be achieved by using SBR and high styrene resins with NR in right proportions. Higher proportions of high styrene resins give products of higher hardness and abrasion resistance and lower density. Silicious fillers such as precipitated silica and aluminum or calcium silicate also give higher hardness, abrasion resistance, and split tear strength.

Microcellular crumbs can be used in considerable quantity along with china clay and whiting to reduce the product cost. Higher proportions of stearic acid (5–10 phr) are normally used in microcellular compounds in order to bring down the decomposition temperature of DNPT type blowing agents (see [Appendix A10](#)). Post-cure oven stabilization of the microcellular sheets, typically at 100°C for 4 h, reduces the delayed shrinkage after cure to a minimum.

2.19 Miscellaneous Processing Techniques

2.19.1 Coating Processes

A coating is thin layer of material used to protect or decorate a substrate. Most often, a coating is intended to remain bonded to the surface permanently, although there are strippable coatings which are

used only to afford temporary protection. An example of the latter type is the strippable hotmelt coating with ethyl cellulose as the binder [46], which is used to protect metal pieces such as drill bits or other tools and gears from corrosion and mechanical abrasion during shipping and handling.

Two of the principal methods of coating substrates with a polymer, namely extrusion coating and calendaring have already been dealt with in this chapter. Other methods of coating continuous webs include the use of dip, knife, brush, and spray. Dip coating, as applied to PVC, has already been described in previous section on plastisols.

In knife coating the coating is applied either by passing the web over a roll running partly immersed in the coating material or by running the coating material onto the face of the web while the thickness of the coating is controlled by a sharply profiled bar (or knife). This technique, also referred to as spreading, is used extensively for coating fabrics with PVC. The PVC is prepared in the form of a paste, and more than one layer is usually applied, each layer being gelated by means of heat before the next layer is added.

Lacquers are a class of coatings in which film formation results from mere evaporation of the solvents(s). The term “lacquer” usually connotes a solution of a polymer. Mixtures of solvents and diluents (extenders which may not be good solvents when used alone) are usually needed to achieve a proper balance of volatility and compatibility and a smooth coherent film on drying. Some familiar examples of lacquers are the spray cans of touch-up paint sold to the auto owner. These are mostly pigmented acrylic resins in solvents together with a very volatile solvent [usually dichlorodifluoromethane (CCl_2F_2)] which acts as a propellant. A typical lacquer formulation for coating steel surfaces contains polymer, pigment, plasticizer (nonvolatile solvent), and volatile solvents.

Latex paints or *emulsion paints* are another class of coatings which form films by loss of a liquid and deposition of a polymer layer. The paints are composed of two dispersions: (1) a resin dispersion, which is either a latex formed by emulsion polymerization or a resin in emulsion form, and (2) a dispersion of colorants, fillers, extenders, etc., obtained by milling the dry ingredients into water. The two dispersions are blended to produce an emulsion paint. Surfactants and protective colloids are added to stabilize the product.

Emulsion paints are characterized by the fact that the binder (polymer) is in a water-dispersed form, whereas in a solvent paint it is in solution form. In emulsion systems the external water phase controls the viscosity, and the molecular weight of the polymer in the internal phase does not affect it, so polymers of high molecular weight are readily utilized in these systems. This is an advantage of emulsion paints.

The minimum temperature at which the latex particles will coalesce to form a continuous layer depends mainly on the T_g . The T_g of a latex paint polymer is therefore adjusted by copolymerization or plasticization to a suitable range. The three principal polymer latexes used in emulsion paints are styrene-butadiene copolymer, poly(vinyl acetate), and acrylic resin.

Although the term “paint” has been used for latex-based systems as well as many others, traditionally it refers to one of the oldest coating systems known—that of a pigment combined with a drying oil, usually a solvent. Drying oils (e.g., linseed, tung), by virtue of their multiple unsaturation, behave like polyfunctional monomers which can polymerize (“dry”) to produce film by a combination of oxidation and free-radical propagation. Oil-soluble metallic soaps are used to catalyze the oxidation process.

Combinations of resins with drying oils yield oleoresinous varnishes, whereas addition of a pigment to a varnish yields an enamel. The combination of hard, wear-resistant resin with softer, resilient, drying-oil films can be designed to give products with a wide range of durability, gloss, and hardness. Another route to obtaining a balanced combination of these properties is the *alkyd resin*, formed from *alcohols* and *acids* (and hence the “alkyd”).

Alkyds are actually a type of polyester resin and are produced by direct fusion of glycerol, phthalic anhydride, and drying oil at 410°F–450°F (210°C–232°C). The process involves an esterification reaction of the alcohol and the anhydride and transesterification of the drying oil. A common mode of operation today is thus to start with the free fatty acids from the drying oil rather than with the triglycerides.

2.19.1.1 Fluidized Bed Coating

Fluidized bed coating is essentially an adaptation of dip coating and designed to be used with plastics in the form of a powder of fine particle size. It is applied for coating metallic objects with plastics. The uniqueness of the process lies in the fact that both thermoplastics and thermosetting resins can be used for the coating. Uniform coating of thicknesses from 0.005 to 0.080 in. (0.13–2.00 mm) can be built on many substrates such as aluminum, carbon steel, brass, and expanded metal. The coating is usually applied for electrical insulation and to enhance the corrosion resistance and chemical resistance of metallic parts.

Low-melting polymers are most appropriate for fluidized beds. Higher melting polymers must have a sufficiently low melt viscosity that the particles can flow and fuse together to form a continuous coating. Thermoplastic polymers in common use include nylon, PVC, acrylics, polyethylene, and polypropylene. Other possible materials are thermoplastic urethane, silicones, EVA, polystyrene, or any other low-melting, low-viscosity polymer. Thermosetting polymers are limited largely to epoxy and epoxy/polyester hybrids since other thermosets, such as phenolic and urea-formaldehyde resins, give off volatile by-products that can create voids in the coating.

The powder resin particles range in size from about 20–200 microns. Particles larger than 200 microns are difficult to suspend. Particles smaller than 20 microns may create excessive dusting and release of particles from the top of the bed.

The actual coating process is uncomplicated; however, achievement of a uniform coating requires considerable skill. The metal object to be coated is powdered resin fluidized by the passage of air through a porous plate. The bed is not heated; only the surface of the object to be coated is hot. As the powder contacts the hot substrate, the particles adhere, melt, and flow together to form a continuously conforming coating. The object is removed from the bed when the desired coating thickness is obtained. On cooling, the coated resin resumes its original characteristics. In the case of a thermosetting resin, additional time at elevated temperature may be required to complete the cure.

The ability of the fluidized bed to continuously conform to and coat parts having unusual shapes and sizes permits a high degree of flexibility in application. This is invaluable to the processor who wishes to coat one-of-a-kind products. In general, the coatings are smooth and glossy, with excellent adhesion to the substrate, providing the hermetic seal necessary for proper maintenance.

Fluidized bed coating is certainly the most efficient method of applying a thick coating in a single step. Thicknesses of 0.1 in. (2.5 mm) or greater are easily attained. Probably the single biggest advantage of powder coating is the nearly 100% utilization of the coating resin, without the hazard or expense of solvents.

Almost all the coatings applied by this process have a definite function, chiefly electrical insulation, but it can be used for applications that simply require a thick coating with powder. Examples of electrical applications include small motor stators and rotors, electronic components (capacitors or resistors), transformer casings, covers, laminations, and busbar. Other items coated using fluidized beds include valve bodies used in chemical industries, refinery equipment, and appliance and pump parts.

2.19.1.2 Spray Coating

Spray coating is especially useful for articles that are too large for dip coating or fluidized bed coating. The process consists of blowing out fine polymer powders through a specially designed burner nozzle, which is usually flame heated by means of acetylene or some similar gas, or it can be heated electrically. Compressed air or oxygen is used as the propelling force for blowing the polymer powder.

2.19.1.3 Electrostatic Spraying

The electrostatic spraying of polymer powders utilizes the principle that oppositely charged particles attract, a principle that has been used for many years in spraying solvent-based paints. In electrostatic spraying, polymer powder is first fluidized in a bed to separate and suspend the particles. It is then transferred through a hose by air to a specially designed spray gun. As the powder passes through the gun,

direct contact with the gun and ionized air applies an electrostatic charge to the particles of powder. The contact area may be a sleeve that extends the length of the gun or merely small pins that extend into the passageway of the powder. For safety the gun is designed for high voltage but low amperage.

The part to be coated is electrically grounded, attracting the charged particles. This produces a more even coating and reduces overspray. Parts to be coated may be preheated, thereby forming the coating immediately, or they may be coated cold as the electrostatic charge will hold the particles in place until heat is applied. Once heat is applied, the particles melt and flow together, forming a continuous protective coating.

Coatings 50–75 microns thick can be applied electrostatically to cold objects and coatings up to 250 microns thick to hot objects. The polymers used in spraying of powders are the same as those used in fluidized beds. The key characteristic for any polymer, thermoplastic or thermoset, applied as a powder is low melt viscosity, which enables polymer particles to flow together and form a continuous coating.

The chief characteristic of electrostatically applied powder polymer is the ability to produce a thin coating. It is the preferred method of producing a coating of 0.001–0.002 in. (0.025–0.050 mm) thickness. It is a continuous process and suited to automated assembly-line production. With a well designed recovery system and fully enclosed spray booth, the process permits full utilization of the powder. The particle size of sprayed powders is smaller than that of powders used in fluidized bed coating. The average particles size is 30–60 microns.

Much of what is termed decorative powder coating is applied by electrostatic spray. Appliances, laboratory instruments, transformer housings, engine parts, and chain-link fences are among the many types of products so coated for decorative purposes.

Coatings that provide electrical insulation are also applied by electrostatic spray. Objects coated include electrical motor armatures and stators, electrical switchgear boxes, and magnet wire. Corrosion-resistant coatings are designed to prevent the corrosion of the underlying substrates. These include pipe, fencing, concrete reinforcing bars, valves, conduit, and pumps. Polymers used for corrosion protection are usually thermosetting, particularly epoxies because of their superior adhesion characteristics.

2.19.2 Powder Molding of Thermoplastics

2.19.2.1 Static (Sinter) Molding

The process is often used with polyethylene and is limited to making open-ended containers. The mold which represents the exterior shape of the product is filled with powder. The filled mold is heated in an oven, causing the powder to melt and thus creating a wall of plastics on the inner surface of the mold. After a specific time to build the required wall thickness, the excess powder is dumped from the mold and the mold is returned to the oven to smooth the inner wall. The mold is then cooled, and the product is removed. The product is strain free, unlike pressure-molded products. In polyethylene this is especially significant if the product is used to contain oxidizing acids.

2.19.2.2 Rotational Molding

Rotational molding (popularly known as rotomolding) is best suited for large, hollow products, requiring complicated curves, uniform wall thickness, a good finish, and stress-free strength. It has been used for a variety of products such as car and truck body components (including an entire car body), industrial containers, telephone booths, portable outhouses, garbage cans, ice buckets, appliance housing, light globes, toys, and boat hulls. The process is applicable to most thermoplastics and has also been adapted for possible use with thermosets.

Essentially four steps are involved in rotational molding: loading, melting and shaping, cooling, and unloading. In the loading stage a predetermined weight of powdered plastic is charged into a hollow mold. The mold halves are closed, and the loaded mold is moved into a hot oven where it is caused to simultaneously rotate in two perpendicular planes. A 4:1 ratio of rotation speeds on minor and major

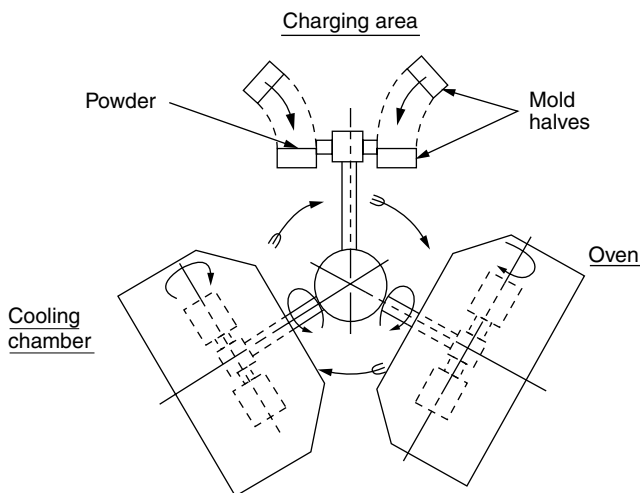


FIGURE 2.78 Basics of continuous-type three-arm rotational molding machine.

axes is generally used for symmetrically shaped objects, but wide variability of ratios is necessary for objects having complicated configurations.

On most units the heating is done by air or by a liquid of high specific heat. The temperature in the oven may range from 500°F–900°F (260°C–482°C), depending on the material and the product. As the molds continue to rotate in the oven, the polymer melts and forms a homogenous layer of molten plastic, distributed evenly on the mold cavity walls through gravitational force (centrifugal force is not a factor). The molds are then moved, while still rotating, from the oven into the cooling chamber, where the molds and contents are cooled by forced cold air, water fog, or water spray. Finally, the molds are opened, and the parts removed. (Rotational molding of plastisol, described earlier, is similar to that described here. However, in this case the plastic is charged in the form of liquid dispersion, which gels in the cavity of the rotating mold during the heating cycle in the oven.)

The most common rotational molding machine in use today is the carousel-type machine. There are three-arm machines consisting of three cantilevered arms or mold spindles extending from a rotating hub in the center of the unit. In operation, individual arms are simultaneously involved in different phases (loading, heating, and cooling) in three stations so that no arms are idle at any time (Figure 2.78).

Modern rotational-molding machines enable large parts to be molded (e.g., 500-lb car bodies and 500-gal industrial containers). For producing small parts an arm of a carousel-type machine may hold as many as 96 cavities.

2.19.2.3 Centrifugal Casting

Centrifugal casting is generally used for making large tube forms. It consists of rotating a heated tube mold which is charged uniformly with powdered thermoplastic along its length. When a tubular molten layer of the desired thickness builds up on the mold surface, the heat source is removed and the mold is cooled. The mold, however, continues to rotate during cooling, thus maintaining uniform wall thickness of the tube. Upon completion of the cooling cycle, the plastic tube, which has shrunk away from the mold surface, is removed, and the process is repeated. Usual tube sizes molded by the process range from 6–30 in. in diameter and up to 96 in. in length.

2.19.3 Adhesive Bonding of Plastics

Adhesives are widely used for joining and assembling of plastics by virtue of low cost and adaptability to high-speed production. They can be subdivided into solvent or dope cements, which are suitable for

most thermoplastics (not thermosets), and monomeric or polymerizable cements which can be used for most thermoplastics and thermosets.

Solvent cements and dope cements function by attacking the surfaces of the adherends so that they soften and, on evaporation of the solvent, will join together. The dope cements, or bodies cements, differ from the straight solvents in that they contain, in solution, quantity of the same plastic which is being bonded. On drying, these cements leave a film of plastic that contributes to the bond between the surfaces to be joined.

Monomeric or polymerizable cements consist of a reactive monomer, identical with or compatible with the plastic to be bonded, together with a suitable catalyst system and accelerator. The mixture polymerizes either at room temperature or at a temperature below the softening point of the thermoplastic being joined. In order to hasten the bonding and to reduce shrinkage, some amount of the solid plastic may also be initially dissolved in the monomer. Adhesives of this type may be of an entirely different chemical type than the plastic being joined. A typical example is the liquid mixture of epoxy resins and hardener which by virtue of the chemical reactivity and hydrogen bonding available from the epoxy adhesive provide excellent adhesion to many materials.

In joining with solvents or adhesives, it is very important that the surfaces of the joint be clean and well matched since poor contact of mating surfaces can cause many troubles. The problem of getting proper contact is aggravated by shrinkage, warpage, flash, marks from ejector pins, and nonflat surfaces.

2.19.3.1 Solvent Cementing

Solvent cementing or solvent welding basically involves softening the bonding area with a solvent or a solvent containing small quantities of the parent plastic, referred to as dope or bodied cement, generally containing less than 15% resin. The solvent or cement must be of such composition that it will dry completely without blushing. Light pressures must be applied to be cemented joint until it has hardened to the extent that there is no movement when released. Structural bonds of up to 100% of the strength of the parent material are possible with this type of bonding.

Table 2.8 gives a list of typical solvents selected as useful for cementing of plastics. A key to selection of solvents in this table is how fast they evaporate: a fast-evaporating solvent may not last long enough for some assemblies, while evaporation that is too slow could hold up production. It may be noted that solvent bonding of dissimilar materials is possible were the materials can be bonded with the same solvents (see Table 2.8).

The Solvent is usually applied by the soak method in which pieces are immersed in the solvent, softened, removed, quickly brought together, and held under light pressure for some time. Areas adjoining the joint area should be masked to prevent them from being etched. For some applications where the surfaces to be cemented fit very closely, it is possible to introduce the cementing solvent by brush, eyedropper, or hypodermic needle into the edges of the joint. The solvent is allowed to spread to the rest of the joint by capillary action.

TABLE 2.8 Typical Solvents for Solvent Cementing of Plastics

Plastics	Solvent
ABS	Methylene chloride, tetrahydrofuran, methyl ethyl ketone, methyl isobutyl ketone
Acetate	Methylene chloride, chloroform, acetone, ethyl acetate, methyl ethyl ketone
Acrylic	Methylene chloride, ethylene dichloride
Cellulosics	Acetone, methyl ethyl ketone
Nylon	Aqueous phenol, solutions of resorcinol in alcohol, solutions of calcium chloride in alcohol
PPO	Methylene chloride, chloroform, ethylene dichloride, trichloroethylene
PVC	Cyclohexane, tetrahydrofuran, dichlorobenzene
Polycarbonate	Methylene chloride, ethylene dichloride
Polystyrene	Methylene chloride, ethylene dichloride, trichloroethylene, methyl ethyl ketone, xylene
Polysulfone	Methylene chloride

2.19.3.2 Adhesive Bonding

Adhesive bonding is a process in which the adhesive acts as an agent to hold two substrates together (as opposed to solvent cementing where the parent materials actually become an integral part of the bond) and the adhesion is chemical.

Table 2.9 gives a list of various adhesives and typical applications in bonding of plastics. This table is not complete, but it does give a general idea of what types of adhesives are used and where. It should be remembered, however, that thousands and thousands of variations of standard adhesives are available off the shelf. The computer may shape up as an excellent selection aid for adhesives. Selection is made according to the combination of properties desired, tack time, strength, method of application, and economics (performance/cost ratio).

The form that the adhesive takes (liquids, mastics, hot melts, etc.) can have a bearing on how and where they are used. The anaerobics, which can give some very high bond strength and are usable with all materials except polyethylene and fluorocarbons, are dispensed by the drop. A thin application of the anaerobics is said to give better bond strength than a thick application.

The more viscous, mastic-type cements include some of the epoxies, urethanes and silicones. Epoxies adhere well to both thermosets and thermoplastics. But epoxies are not recommended for most polyolefin bonding. Urethane adhesives have made inroads into flexible packaging, the shoe industry, and vinyl bonding. Polyester-based polyurethanes are often preferred over polyether systems because of their higher cohesive and adhesive properties. Silicones are especially recommended where both bonding and sealing are desired.

Hot melts—100% solids adhesives that are heated to produce a workable material—are based on polyethylene, saturated polyester or polyamide in chunk, granule, pellet, rope, or slug form. Saturated polyesters are the primary hot melts for plastics; the polyethylenes are largely used in packaging; polyamides are used most widely in the shoe industry. Application speeds of hot melts are high and it pays to consider hot melts if production requirements are correspondingly high.

Pressure sensitives are contact-bond adhesives. Usually rubber based, they provide a low-strength, permanently tacky bond. They have a number of consumer applications (e.g., cellophane tape), but they are also used in industrial applications where a permanent bond is not desirable or where a strong bond may not be necessary. The adhesive itself is applied rapidly by spray. Assembly is merely a matter of pressing the parts together.

Film adhesives require an outside means such as heat, water, or solvent to reactivate them to a tacky state. Among the film types are some hot melts, epoxies, phenolics, elastomers, and polyamides. Film adhesives can be die cut into complicated shapes to ensure precision bonding of unusual shapes. Applications for this type of adhesive include bonding plastic bezels onto automobiles, attaching trim to both interiors and exteriors, and attaching nameplates on luggage.

While most plastics bond without trouble once the proper adhesive has been selected, a few, notably polyolefins, fluorocarbons and acetals, require special treatment prior to bonding. Untreated polyolefins adhere to very few substrates (a reason that polyethylene is such a popular material for packaging adhesives). Their treating methods include corona discharge, flame treating (especially for large, irregular-shaped articles), and surface oxidation by dipping the articles in a solution of potassium dichromate and sulfuric acid. Fluorocarbons can be prepared for bonding by cleaning with a solvent such as acetone and then treating with a special etching solution. For acetals, one pretreatment method involves immersing articles in a special solution composed mainly of perchloroethylene, drying at 120°C (250°F), rinsing, and then air drying.

2.19.3.3 Joining of Specific Plastics

The same basic handling techniques apply to almost all thermoplastic materials. In the following section, however, a few thermoplastics will be treated separately, with mention of the specific cements most suitable for each. The section on acrylics should be read in connection with the cementing of any other thermoplastics.

TABLE 2.9 Typical Adhesives for Bonding Plastics

	ABS	Acetal	Acrylic	Cellulosics	Fluorocarbons	Nylon	PVC	PC	PE	PP	PS	MF	PF	Polyesters	PU
Metals	10	3,10	2,3	2,3	9,10	2,10	2,3,7,10,13,14	10	2,12	1	12	3,14	2	4	3,4
Paper	—	3,10	—	—	9,10	3	—	13	—	1	4,12,13	—	—	—	4,13
Wood	10	10	2,3	3	10	2,3	3,10,13	10,13	2	1	12,13	2,3	2	2	13
Rubber	10	3	1–4	1–4	10	2	3,4,7	4,13	2	1	5	2,3,14	2,3	1,4	4,13
Ceramics	—	10	2,3	3	10	3,10	3,4	10,13	2	1	—	2	2	2	3
ABS	10,14	2,4,6,10	2,4,6,10	—	—	8,10	10	4,10	10	—	—	—	—	—	—
Acetal	2,4,6,10	3,10	10	—	10	10	10	—	—	—	—	—	10	—	—
Acrylic	2,4,6,10	2,4,6,10	15	—	10	2,3,4,9	3,4,6,10	—	—	—	—	—	4,8,10	10	4,10
Cellulosic	—	—	—	3,4,13	10	2,3,7,9	10	—	—	—	—	—	10	—	—
Fluorocarbons	—	10	—	—	9,10	—	10	—	10	—	10	—	—	—	10
Nylon	8,10	8,10	2,3,7,9	2,3,7,9	—	2,9,10,13	—	—	—	—	—	8,10	8,10,14	8,10	—
PVC	10	10	3,4,6,10	—	10	—	3,4,6,13	—	—	—	—	—	4,7	10	—
PC	10	—	—	—	—	—	3,4,6,13	15	—	—	—	—	—	—	—
PE	10	—	—	—	10	—	—	—	10,12	—	—	—	—	—	—
PP	—	—	—	—	—	—	—	—	—	10,12	—	—	—	—	—
PS	—	—	—	—	10	—	—	—	—	—	4,5,10,12,13	—	4,10,14	—	—
MF	—	—	—	—	—	—	—	—	—	—	—	2,3,10,12,13	—	—	—
PF	10,14	14	4,8,10	10	—	4,7	—	—	—	4,10	3,8,10,11	2–4,10,12,14	—	—	—
Polyester	—	—	10	10	—	—	10	—	—	—	—	—	—	3,10,12,13	—
PU	—	—	4,10	—	10	—	—	—	—	—	—	—	—	—	3,4,10,13

Elastomeric: 1, Natural rubber. 2, Neoprene. 3, Nitrile. 4, Urethane. 5, Styrene-butadiene. Thermoplastic: 6, Poly(vinyl acetate). 7, Polyamide. Thermosetting: 8, Phenol-formaldehyde. 9, Resorcinol, Phenol-resorcinol/formaldehyde. 10, Epoxy. 11, urea-formaldehyde. Resin: 12, Phenolic-poly(vinyl butyral). 13, Polyester. Other: 14, Cyanoacrylate. 15, Solvent.

Source: Adapted from O'Rinda Trauernicht, J. 1970. *Plastics Technology*, Reinhold Publishing, New York.

2.19.3.3.1 Cast Acrylic Sheeting

Articles of considerable size and complexity can be fabricated from methyl methacrylate plastics by joining sections together by solvent welding. The technique described here applies to cast sheeting. With articles made from methyl methacrylate molding powders or extruded rod, tubing or other shapes, joining is generally not as satisfactory as with cast sheeting.

With care and practice, the transparency of acrylic resin can be retained in joints with the formation of a complete union of the two surfaces brought into contact. Usually one of the two surfaces to be joined is soaked in the cementing solvent until a soft, swollen layer (cushion) has been formed upon it. This soft surface is then pressed against the surface to be attached and held in contact with it so that the excess solvent contained in the soaked area softens it also.

For some purposes, it may be desirable to dissolve clean savings of methyl methacrylate resin in the solvent in order to raise its viscosity so that it can be handled like glue.

The most universally applicable type of solvent cement is the polymerizable type, comprising a mixture of solvent and catalyzed monomer. These are mobile liquids, volatile, rapid in action, and capable of yielding strong sound bonds. An example of these is a 40–60 mixture of methyl methacrylate monomer and methylene chloride. Before using this cement, 1.2 grams of benzoyl peroxide per pint of solvent, should be added. Heat treatment or annealing of joints made with solvent cements is highly desirable because it greatly increases the strength of the joint.

2.19.3.3.2 Cellulosics

The cements used with cellulosic plastics are of two types: (1) solvent type, consisting only of a solvent or a mixture of solvents; (2) dope type, consisting of a solution of the cellulosic plastic in a solvent or mixture of solvents.

Acetone and mixture of acetone and methyl “cellosolve” are commonly used as solvent cements for cellulose acetate. Acetone is a strong solvent for the plastic, but evaporates rapidly. The addition of methyl “cellosolve” retards the evaporation, prevents blushing, and permits more time for handling the parts after application of the cement.

A cement of the dope type leaves upon drying a film of plastic that forms the bond between the surfaces to be joined. These cements are generally used when an imperfect of the parts requires filling. A typical composition of the dope-type cement for cellulose acetate is:

	Parts by Weight
Cellulose acetate	130
Acetone	400
Methyl “cellosolve”	150
Methyl “cellosolve” acetate	50

Other cellulosics, cellulose acetate butyrate and propionate are cemented in accordance with the technique described for cellulose acetate. In the case of dope cements, the plastic to be dissolved in solvents is cellulose propionate. Similarly for ethyl cellulose plastic, the strongest bonds are made by solvents or by solvents bodied with ethyl cellulose plastic.

2.19.3.3.3 Nylon

The recommended cements for nylon-to-nylon bonding are generally solvents, such as aqueous phenol, solutions of resorcinol in alcohol, and solutions of calcium chloride in alcohol, sometimes “bodied” by the inclusion of nylon in small percentages.

Aqueous phenol containing 10–15% water is the most generally used cement for bonding nylon to itself. The bond achieved by use of this cement is water resistant, flexible, and has strength approaching that of the nylon.

Calcium–chloride–ethanol solution bodied with nylon is recommended for nylon-to-nylon joints where there is possibility of contact with foods or where phenol or resorcinol would be otherwise objectionable.

For bonding nylon to metal and other materials, various commercial adhesives, especially those based on phenol-formaldehyde and epoxy resins, are sometimes used. Epoxy adhesives (in two-part systems), for example, have been used to produce satisfactory joints between nylon and metal, wood, glass and leather.

2.19.3.3.4 Polycarbonate

Solvent cementing of parts of polycarbonate may be effected by the use of a variety of solvents or light solutions of polycarbonate in solvents. Methylene chloride, a 1–5% solution of polycarbonate in methylene chloride, and a mixture of methylene chloride and ethylene dichloride (with a maximum of 40% ethylene dichloride) are commonly recommended.

Solvent should be applied to only one of the bonding surfaces while the other half remains dry and ready in the clamping fixture. As soon as the two parts have been put together, pressure should be applied immediately. Pressure between 200 and 600 psi is suggested for best results. Holding time in the pressure fixture is approximately 1–5 min, depending on the size of the bonding area.

For bonding molded parts of polycarbonate to other plastics, glass, wood, aluminum, brass, steel, and other materials, a wide variety of adhesives can be used. Generally, the best results are obtained with solventless materials, such as epoxies and urethanes.

2.19.3.3.5 Polyethylene

The good solvent resistance of polyethylene and other olefins precludes the use of solvent-type cements. Several commercial rubber-type adhesives produce moderate adhesion with polyethylene that has been surface treated. One technique for surface treatment is to dip polyethylene in a chromic acid bath (made up of concentrated sulfuric acid 150 parts by weight, water 12 parts, and potassium dichromate 7.5 parts) for about 30 sec at 70°C. The parts are rinsed with water after this treatment. Still another effective surface treatment for producing cementable surfaces on polyethylene is electrical discharge. The open oxidizing flame method is also used extensively for this purpose.

2.19.3.3.6 Polystyrene

Complex assemblies of polystyrene, usually molded in section, may be joined by means of solvents and adhesives. Polystyrene is soluble in a wide variety of solvents. According to their relative volatilities they may be divided into three groups—fast drying, medium drying, and slow drying.

Methylene chloride, ethylene dichloride, and trichloroethylene are some of the fast-drying solvents that produce strong joints. However, they are unsatisfactory for transparent articles of polystyrene because they cause rapid crazing. “Medium-drying” solvents such as toluene, perchloroethylene, and ethyl benzene that have higher boiling temperature are less apt to cause crazing.

High-boiling or “slow-drying” solvents such as amylbenzol and 2-ethylnaphthalene often require excessive time for development of sufficient bond strength, but they will not cause crazing to appear so quickly. Up to 65% of a fast- or medium-drying solvent may be added to a slow-drying solvent to speed up the development of initial tack without greatly reducing the time before crazing appears.

A bodied, or more viscous, solvent may be required by certain joint designs and for producing airtight or watertight seals. These are made by dissolving usually 5%–15% of polystyrene by weight in a solvent. Solvent-based contact cements provide the strongest bond between polystyrene and wood. These adhesives all have a neoprene (polychloroprene) base and a ketonic-aromatic solvent system.

2.19.3.3.7 Poly(Vinyl Chloride) and Copolymers

On account of the relative insolubility of PVC and the markedly increased effect of solvents with the increasing content of vinyl acetate in the copolymer resins, there exists among the vinyl chloride-acetate copolymer system a great diversity of composition and of ability to be cemented by solvents.

The copolymer resins are most rapidly dissolved by the ketone solvents, such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone. Propylene oxide also is a very useful solvent in hastening solution of copolymer resins, especially those of high molecular weight, and of straight PVC. This solvent penetrates the resins very rapidly and, in amounts up to about 20–25%, improves the “bite”

into the resin. The chlorinated hydrocarbons also are excellent solvents for the vinyl chloride-vinyl acetate copolymer resins, and are suitable for use in cements.

2.19.3.3.8 Thermosetting Plastics

Adhesive bonding is, for various reasons, the logical method of fastening or joining cross-linked and reinforced thermoset plastics of themselves, or to other materials. Since most thermoset plastics are quite resistant to solvents and heat, heat-curing solvent-dispersed adhesives may be used. Such adhesives consist of reactive or thermosetting resins (e.g., phenolics, epoxies, urea-formaldehydes, alkyds, and combinations of these), together with compatible film-formers such as elastomers or vinyl-aldehyde condensation resins. Isocyanates are frequently added as modifiers to improve specific adhesion to surfaces that are difficult to bond. These adhesives may be applied not only in solvent-dispersed form, but also in the form of film, either unsupported, or supported on fabric, glass-mat, and so forth.

A great many of outstanding adhesive formulations are based on epoxy resins. A broad spectrum of adhesive formulations with a wide range of available properties have resulted from the use of polymeric hardeners such as polyamides and polyamines, phenolics, isocyanates, alkyds, and combinations of amines with polysulfide elastomers, and the “alloying” of the epoxy with compatible polymeric film-formers, such as poly(vinyl acetate) and certain elastomers.

In cemented assemblies of thermoset plastics and metals, where structural strength is generally desired, the adhesive must be more rigid than those used for bonding plastic to plastic, i.e., one with modulus, strength, and coefficient of thermal expansion between those of the plastic and the metal. In many cases, such adhesives are stronger than the plastic itself.

2.19.4 Welding

Often it is necessary to join two or more components of plastics to produce a particular setup or to repair a broken part. For some thermoplastics solvent welding is applicable. The process uses solvents which dissolve the plastic to provide molecular interlocking and then evaporate. Normally it requires close-fitting joints. The more common method of joining plastics, however, is to use heat, with or without pressure. Various heat welding processes are available. Those processes in common commercial use are described here.

2.19.4.1 Hot-Gas Welding

Hot-gas welding, which bears a superficial resemblance to welding of metals with an oxyacetylene flame, is particularly useful for joining thermoplastic sheets in the fabrication of chemical plant items, such as tanks and ducting. The sheets to be joined are cleaned, beveled, and placed side by side so that the two beveled edges form a V-shaped channel. The tip of a filler rod (of the same plastic) is placed in the channel, and both it and the adjacent area of the sheets are heated with a hot-gas stream (200–400°C) directed from an electrically heated hot-gas nozzle ([Figure 2.79a](#)), which melts the plastics. The plastics then fuse and unite the two sheets. The hot gas may be air in PVC welding, but for polyethylene an inert gas such as nitrogen must be used to prevent oxidation of the plastics during welding.

2.19.4.2 Fusion Welding

Fusion or hot-tool welding is accomplished with an electrically heated hot plate or a heated tool (usually of metal), which is used to bring the two plastic surfaces to be joined to the required temperature. The polyfusion process for joining plastic pipes by means of injection-molded couplings is an example of this type of welding. The tool for this process is so shaped that one side of it fits *over* the pipe while the other side fits into the coupling. The tool is heated and used to soften the outside wall of the pipe and the inside wall of the coupling. The pipe and coupling are firmly pressed together and held until the joint cools to achieve the maximum strength of the weld. The tool is chrome plated to prevent the plastic sticking to its surfaces.

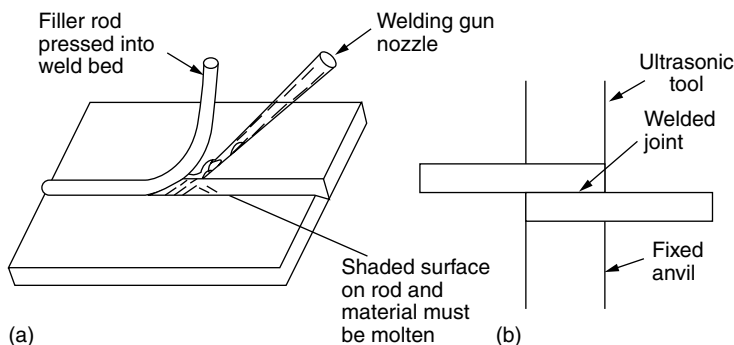


FIGURE 2.79 Welding of plastics: (a) hot-gas welding; (b) ultrasonic contact welding.

2.19.4.3 Friction Welding

In friction or spin-welding of thermoplastics, one of the two pieces to be jointed is fixed in the chuck of a modified lathe and rotated at high speed while the other piece is held against it until frictional heat causes the polymer to flow. The chuck is stopped, and the two pieces are allowed to cool under pressure. The process is limited to objects having a circular configuration. Typical examples are dual-colored knobs, molded hemispheres, and injection-molded bottle halves.

2.19.4.4 High-Frequency Welding

Dielectric or high-frequency welding can be used for joining those thermoplastics which have high dielectric-loss characteristics, including cellulose acetate, ABS, and PVC. Obviously, polyethylene, polypropylene, and polystyrene cannot be welded by this method. The device used for high-frequency welding is essentially a radio transmitter operated at frequencies between 27 and 40 MHz. The energy obtained from the transmitter is directed to electrodes of the welding apparatus. The high-frequency field causes the molecules in the plastic to vibrate and rub against each other very fast, which creates frictional heat sufficient to melt the interfaces and produce a weld.

2.19.4.5 Ultrasonic Welding

In ultrasonic welding the molecules of the plastic to be welded are sufficiently disturbed by the application of ultrahigh-frequency mechanical energy to create frictional heat, thereby causing the plastics to melt and join quickly and firmly.

The machinery for ultrasonic welding consists of an electronic device which generates electrical energy at 20/50 kHz/sec and a transducer (either magnetostrictive or piezoelectric) to convert the electrical energy to mechanical energy. In the contact-welding method (Figure 2.79b) the ultrasonic force from the transducer is transmitted to the objects (to be welded) through a tool or “horn,” generally made of titanium. The amplitude of the motion of the horn is from 0.0005 to 0.005 in. (0.013–0.13 mm) depending on the design. The method is generally used for welding thin or less rigid thermoplastics, such as films, or sheets of polyethylene, plasticized PVC, and others having low stiffness.

2.20 Decoration of Plastics

Commercial techniques for decorating plastics are almost as varied as plastics themselves. Depending on end-use applications or market demands, virtually any desired effect or combination of effects, shading of tone, and degree of brightness can be imparted to flexible or rigid plastics products.

The primary decorating technique is raw-materials coloring achieved at the compounding stage. Although most thermoplastics are produced in natural white or colorless transparent form, color is usually added by directly blending colorants into the base resin prior to the processing stage. These colorants (or color concentrates) are available in a wide range of stock shades with precise tinctorial values.

Colors can also be matched to exact customer specifications and these specifications kept in computer memory to ensure batch-to-batch or order-to-order consistency. Color blending can also be utilitarian, as in color-coded wire- and cable-sheathing.

Besides basic raw-materials coloring, mentioned above, designers have a large palette of decorating media at their disposal. Plastics can be decorated in various ways, which include painting processes, direct printing, transfer decoration, in-mold decoration, embossing, vacuum metallizing, sputtering, and electroplating. Most of these processes require bonding other media, such as inks, enamels, and other materials to the plastics to be decorated.

Some plastics, notably polyolefins and acetals, are, however, highly resistant to bonding and need separate treatment to activate the surface. Commonly used treatment processes are flame treatment, electronic treatments such as corona discharge and plasma discharge, and chemical treatment.

In flame treatment, plastic objects such as bottles and film are passed through an oxidizing gas flame. Momentary contact with the flame causes oxidation of the surface, which makes it receptive to material used in decorating the product.

In the corona discharge process the plastic film to be treated is allowed to pass over an insulated metal drum beneath conductors charged with a high voltage. When the electron discharge ("corona") between the charged conductors and the drum strikes the intervening film surface, oxidation occurs and makes the surface receptive to coatings. Molded products are also treated in a similar manner, often by fully automatic machinery.

In the plasma process [48], air at low pressure is passed through an electric discharge, where it is partially dissociated into the plasma state and then expanded into a closed vacuum chamber containing the plastic object to be treated. The plasma reacting with the surfaces of the plastic alters their physicochemical characteristics in a manner that affords excellent adhesion to surface coatings. The process can be used for batch processing of plastics products, including films which may be unreeled in the vacuum chamber for treatment.

Acetal resin products are surface treated by a chemical process consisting of subjecting the product to a short acid dip that results in an etched surface receptive to paint.

2.20.1 Painting

Virtually all plastics, both thermoplastic and thermosetting, can be painted, with or without priming or other preliminary preparation procedures. The process, however, requires special consideration of the resin-solvent system to achieve adhesion, adequate covering, and chemical resistance. Painting operations have the advantage of being as simple or as sophisticated as the application may dictate.

Plastics parts or materials can be coated manually by brushing, dipping, hand-spray painting, flow coating or roller coating; they can be automatically spray-painted with rotating or reciprocating spray guns, and electro-statically painted using a conductive precoating procedure.

Painting operations have the advantage of offering almost unlimited color options as well as great variety of surface finishes and final surface properties to meet such needs as gloss, UV resistance, abrasion resistance, and chemical resistance.

2.20.2 Printing

The primary printing presses used in plastics are gravure printing, flexography, silk-screen printing, and pad printing.

2.20.2.1 Gravure Printing

Gravure printing is a process that requires the use of an engraved metal cylinder or roller. Rotogravure is thus an appropriate title for this printing process. The engraving or etching process on the surfaces of the metal cylinder results in recessed areas that pick up ink or liquid coatings from a reservoir. With proper

formulation of printing ink, the gravure process can be applied to a great variety of plastic substrates. Virtually all thermoplastic film or sheet applications are printable by this process.

A good example of the capabilities of the gravure process is the printing of woodgrain patterns on carrier foil for use in hot-stamping applications (described later). Woodgrain patterns may require the application of several coatings to achieve the proper effect. Several engraved cylinders can be used in sequence for continuous printing.

2.20.2.2 Flexography

Flexography uses a flexible printing plate, typically a metal-silicone rubber-bonded combination with the rubber surface processed to leave the printing surface raised over the back-ground area. The raised and recessed areas on the surface can be fabricated through photographic etching and/or engraving. After transferring the ink from a reservoir through a roller-doctor blade system onto the curved flexible plate, the ink is transferred off the raised portions to the material to be printed.

The process is suitable for a variety of applications, ranging from simple label film to decoration on molded parts such as plaques, medallions or wall tile. However, the flexible printing plates used in flexography do not permit the very fine detail that can be achieved on metal surfaces such as used in gravure printing. There are also limitations to the size and shape of articles that can be printed.

2.20.2.3 Screen Process Printing

The process derived its name from the use of silk cloth or silk screen in the transfer of printing ink to articles to be printed. Integral to the process is the use of a suitable open-weave cloth or screen (silk is still commonly but not exclusively used) stretched over a framework. Screens made of nylon or other synthetic material are often employed, as also stainless steel or other metallic screens. The stretched screen is selectively coated through the use of a stencil corresponding to an art copy of the image to be printed (see “Silkscreen Printing” in [Chapter 5](#)); this coated (closed) area resists the passage of printing ink, which can only penetrate through the uncoated (open) areas of the screen. There are various ways to prepare the screen for printing, other than stenciling.

Polyolefins such as polyethylene and polypropylene must be surface treated before being printed. The most effective way is in an integrated machine where surface treatment takes place right before printing. A time lapse will mean that the treatment will lose some of its effect. Three methods are used; flame treatment, corona discharge, and chemical treatment. Flame treatment is considered the most practical and most widely used.

2.20.2.4 Pad Printing

Pad printing uses printing principles and techniques from letterpress and flexography. The uniqueness of the process has to do with the use of a smooth silicone pad that picks up ink impression from an engraved or etched plate and transfers it to the product to be decorated. The engraved plate, known as a cliché, is produced in a manner similar to that of printing plates for offset or gravure roller printing.

The silicone pickup pad can be designed to meet almost any shape and configuration of the product part. This ability has prompted tremendous growth in pad printing. An additional capability of the process is that it can print several colors and impressions within one cycle of operation. Coatings can be layered when wet to accomplish multicolor designs with very accurate registration and impression quality.

2.20.3 Hot Stamping

Hot stamping is one of the original methods of decorating plastics materials. Though familiarly known as hot stamping, the terminology “coated foil transferring” might be more appropriate since in this process the printed coating on a carrier film is transferred onto a plastic surface. Secure adhesion is accomplished with the use of heat, pressure, and time under controlled conditions.

The key to the process is the use of a carrier film (usually a polycarbonate, polyester, or cellophane) upon which various coatings provide the desired decorative effect. The coated foil is placed over the

plastic to be decorated, and a heated die forces the foil onto the plastic. The proper control of heat, pressure, and time transfers the coating off the carrier foil onto the plastic.

The hot-stamping process is a versatile tool for plastics decoration. A wide variety of coatings can be deposited on the carrier film which allows the process to be used on almost any thermoplastic material and many thermosets. Metallic effects can be imparted by depositing microthin coatings of gold or silver or chrome; multiple coatings can be applied to the carrier film to achieve such effects as woodgraining, marbleizing, or multicolored designs. Three-dimensional decorative effects can also be achieved by embossing the surface of the carrier medium coating.

2.20.4 In-Mold Decorating

As the name implies, in-mold decorating is a process in which a predecorated overlay (film), or decal, is placed in the mold, where the decorated element is fused to the molded part during the heating/cooling cycles of the molding operation. Since the decorated coating is bonded between the plastic part and the film (which will be the exterior surface), thus forming an integral part of the product, it produces one of the most durable and permanent decorations. High-quality melamine dinnerware is decorated by this method, and so are a host of other household and hardware plastics goods.

In-mold decoration can be done with either injection molding of thermoplastics or compression molding of thermosets. Thermosetting plastics are decorated with a two-stage process. For melamine products, for example, the mold is loaded with the molding powder in the usual manner and closed. It is opened after a partial cure, and the decorative “foil” or overlay is placed in position.

The mold is then closed again, and the curing cycle is completed. The overlay consists of a cellulose sheet having printed decoration and covered with a thin layer of partially cured clear melamine resin. During the molding cycle the overlay is fused to the product and becomes a part of the molding. The process is relatively inexpensive, especially when a multicolor decoration is required.

For in-mold decoration of thermoplastic products, single-stage process is used. The foil or overlay is thus placed in the mold cavity prior to the injection of the polymer. It is held in place in the mold by its inherent static charge. Shifting is prevented during molding inducing an additional charge by passing the wand of an electronic static charging unit over the foil after it is properly positioned.

The overlay, in all cases, is a printed or decorated film (0.003–0.005 in. thick) of the same polymer. Thus, polystyrene film is used for a polystyrene product, and polypropylene film for a polypropylene product. A similar procedure may also be used for decorating blow-molded products.

2.20.5 Embossing

Embossing is used for producing a tactile texture or pattern on plastics sheet or film. As the process involves the use of heat and pressure to texture a semifinished substrate, embossing is largely limited to thermoplastic materials. However, it can be adapted to thermoset composites, such as melamine-impregnated sheet stock.

Embossing is most commonly done with a two-roller system, in which one roller carries the embossing pattern and the other provides the essential pressure backup and feeding actions. Texture or pattern can be applied to the embossing or surface roller through a variety of processes, including conventional engraving, chemical engraving, etching, and laser cutting.

Embossing can also be performed without rollers, e.g., using textured aluminum foil in one-time use, or stainless steel plates with engraved textures can be used in the press cycle time and again, offering multiple impression economies.

Embossing is most frequently used as a method of decorating nonslip packaging materials, vinyl wall coverings, furniture laminates, building-panel laminates, textured foil for hot stamping, and other applications where the innate quality of three-dimensional printing is of value.

2.20.6 Electroplating

Electroplating is a chemical process for depositing heavy metals on plastics to achieve decorative effects and/or upgraded functionality. Since plastics are nonconductors of electricity, electroplating requires that the surface be properly conditioned and sensitized to receive metallic coatings. The principle of electroplating is to electrically conduct metal atoms such as copper, nickel and chrome off anodes placed within the plating baths through the plating solutions and onto the plastic production part. The target, i.e., the production part, acts as a cathode via connection to conductive plating racks, the part being attached to the plating rack with metal holding devices, spring-loaded contacts or prongs. The point of contact between the plating rack and the plastic part forms the continuity of the current flow from anode through the solution onto the plastic part.

The process of electroplating begins with the plastic part attached to the plating rack being subjected to preplate procedure, which is designed to create a surface on the plastic parts that will develop a bond between the plastic and the first nickel or copper deposit. These initial deposits are extremely thin, in the micron (10^{-6} mm) range. This first deposit is designed to increase conductivity uniformly over the plastic surface.

When preplating is completed (and the plastic articles have a conductive coating), it is possible to proceed to the electroplating operation, which is very similar to conventional electroplating on metal.

Electroplating of plastic products provides the high-quality appearance and wear resistance of metal combined with the light weight and corrosion resistance of plastics. Plating is done on many plastics, including phenolic, urea, ABS, acetal, and polycarbonate. Many automotive, appliance, and hardware uses of plated plastics include knobs, instrument cluster panels, bezel, speaker grilles, and nameplates. In marine searchlights zinc has been replaced by chrome-plated ABS plastics to gain lighter weight, greater corrosion resistance, and lower cost. An advantage of plastics plating is that, unlike metal die castings, which require buffing in most cases after plating, plastics do not ordinarily require this extra expensive operation. The use of plated plastics also affords the possibility of obtaining attractive texture contrasts.

2.20.7 Vacuum Metallizing

Vacuum metallizing is a process whereby a bright thin film of metal is deposited on the surface of a molded product or film under high vacuum. The metal may be gold, silver, or most generally, aluminum. The process produces a somewhat delicate surface compared to electroplating. The metallizing process can be used on virtually all properly (surface) prepared thermoplastic and thermosetting materials.

Small clips of the metal to be deposited are attached to a filament. When the filament is heated electrically, the clips melt and, through capillary action, coat the filament. An increased supply of electrical energy then causes vaporization of this metal coating, and plating of the plastic product takes place.

To minimize surface defects and enhance the adhesion of the metal coating, manufacturers initially give the plastics parts a lacquer base coat and dry in an oven. The lacquered parts are secured to a rack fitted with filaments, to which are fastened clips of metal to be vaporized. The vaporization and deposition are accomplished at high vacuum (about 1/2 micron). The axles supporting the part holding the fixtures are moved so as to rotate the parts during the plating cycle to promote uniform deposition. The thickness of the coating produced is about 5×10^{-6} in. (127 nm).

After the deposition is completed, the parts are removed and dipped or sprayed with a top-coat lacquer to protect the metal from abrasion. Color tones, such as gold, copper, and brass may be added to this coating if desired.

Vacuum metallizing of polymer films, such as cellulose acetate, butyrate, and Mylar, is performed in essentially the same way. Film rolls are unreel and rewound during the deposition process to metallize the desired surface. A protective abrasion-resistant coating is then applied to the metallized surface in an automatic coating machine.

Vacuum metallizing is a versatile process used in a great variety of applications. Examples range from highly decorative cosmetic closures to automotive grilles and instrument clusters. Vacuum metallized plastic parts can replace metal parts with large saving in manufacturing costs and weight. The process can also serve functional needs, such as lamp reflectors or diffusion grids for overhead fluorescent lighting. Vacuum metallizing on interior surfaces of computer or communication equipment provides a degree of radio frequency interference shielding.

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3

Plastics Properties and Testing

3.1 Introduction

There are two stages in the process of becoming familiar with plastics. The first is rather general and involves an introduction to the unique molecular structures of polymers, their physical states, and transitions which have marked influence on their behavior. These have been dealt with in [Chapter 1](#). The second stage, which will be treated in this chapter, is more specific in that it involves a study of the specific properties of plastics which dictate their applications. Besides the relative ease of molding and fabrication, many plastics offer a range of important advantages in terms of high strength/weight ratio, toughness, corrosion and abrasion resistance, low friction, and excellent electrical resistance. These qualities have made plastics acceptable as materials for a wide variety of engineering applications. It is important therefore that an engineer be aware of the performance characteristics and significant properties of plastics.

In this chapter plastics have been generally dealt with in respect to broad categories of properties, namely, mechanical, electrical, thermal, and optical. In this treatment the most characteristic features of plastic materials have been highlighted.

An important facet of materials development and proper materials selection is testing and standardization. The latter part of this chapter is therefore devoted to this aspect. It presents schematically (in simplified form) a number of standard test methods for plastics, highlighting the principles of the tests and the properties measured by them.

3.2 Mechanical Properties

Several unfamiliar aspects of material behavior of plastic need to be appreciated, the most important probably being that, in contrast to most metals at room temperature, the properties of plastics are time dependent [1-4]. Then superimposed on this aspect are the effects of the level of stress, the temperature of the material, and its structure (such as molecular weight, molecular orientation, and density). For example, with polypropylene an increase in temperature from 20 to 60°C may typically cause a 50% decrease in the allowable design stress. In addition, for each 0.001 g/cm³ change in density of this material there is a corresponding 4% change in design stress. The material, moreover, will have enhanced strength in the direction of molecular alignment (that is, in the direction of flow in the mold) and less in the transverse direction.

Because of the influence of so many additional factors on the behavior of plastics, properties (such as modulus) quoted as a single value will be applicable only for the conditions at which they are measured. Properties measured as single values following standard test procedures are therefore useful only as a

means of quality control. They would be useless as far as design is concerned, because to design a plastic component it is necessary to have complete information, at the relevant service temperature, on the time-dependent behavior (viscoelastic behavior) of the material over the whole range of stresses to be experienced by the component.

3.2.1 Stress and Strain

Any force or load acting on a body results in stress and strain in the body. Stress represents the intensity of the force at any point in the body and is measured as the force acting per unit area of a plane. The deformation or alteration in shape or dimensions of the body resulting from the stress is called *strain*. Strain is expressed in dimensionless units, such as *cm/cm*, *in./in.*, or in *percentage*.

Corresponding to the three main types of stress—tensile, compressive, and shear—three types of strain can be distinguished. Thus, *tensile strain* is expressed as elongation per unit length (Figure 3.1a),

$$\varepsilon = \Delta\ell/\ell_0 = (\ell - \ell_0)/\ell_0 \quad (3.1)$$

and *compressive strain* as contraction per unit length (Figure 3.1b),

$$\varepsilon = \Delta\ell/\ell_0 = (\ell_0 - \ell)/\ell_0 \quad (3.2)$$

If the applied force or load, F , is tensile or compressive, the resulting tensile or compressive stress, σ , is defined by

$$\sigma = F/A \quad (3.3)$$

where A is the cross-sectional area perpendicular to the direction in which the force acts (Figure 3.1a).

The shearing stress is defined by a similar equation

$$\tau = F_s/A \quad (3.4)$$

where F_s is the shearing force acting on an area A , which is parallel to the direction of the applied force (Figure 3.1c).

Shear strain is measured by the magnitude of the angle representing the displacement of a certain plane relative to the other, due to the application of a pure shear stress, such as α in Figure 3.1c. The corresponding shear strain γ may be taken equal to the ratio aa'/ab ($=\tan \alpha$). A shear strain is produced in torsion, when, for example, a circular rod is twisted by tangential forces, as shown in

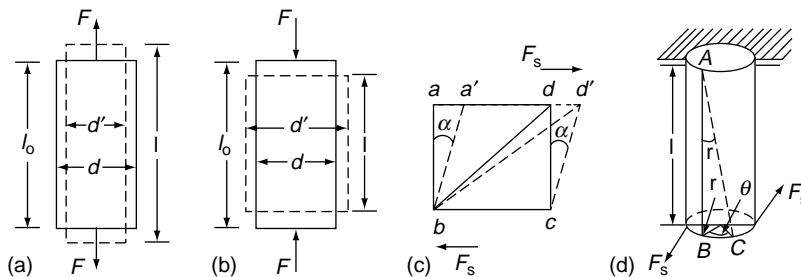


FIGURE 3.1 (a) Tensile or longitudinal strain, $\varepsilon = (\ell - \ell_0)/\ell_0$. (b) Compressive strain, $\varepsilon = (\ell_0 - \ell)/\ell_0$. (c) Shear strain, $\gamma = aa'/ab$. (d) Shear strain in torsion $\gamma = r\theta/\ell$.

Figure 3.1d. For small deformations the shear strain, γ , can be calculated from the triangle ABC

$$\gamma = BC/AB = r\theta/\ell \quad (3.5)$$

where r is the radius and θ is the angle of twist.

An ideal elastic material is one which exhibits no time effects. When a stress is applied the body deforms immediately, and it recovers its original dimensions completely and instantaneously when the stress is removed. When the ideal elastic body is subjected to tensile (or compressive) stress, the proportionality is expressed as

$$\sigma = E \cdot \varepsilon \quad (3.6)$$

where σ is the applied stress (tensile or compressive) in lbf/in.², kgf/cm² or other appropriate units of force per unit cross-sectional area (Equation 3.3), ε is the axial strain (Equation 3.1 and Equation 3.2), and E is the modulus of elasticity, commonly known as the Young's modulus. The proportionality law as defined above is known as Hooke's law.

Likewise, if the ideal solid is subjected to a shear stress (τ), then the shear strain (γ) developed as a function of stress applied is given by the expression

$$\tau = G \cdot \gamma \quad (3.7)$$

Here, the proportionality constant G is known as the shear modulus, also called the modulus of rigidity.

The elastic constants in tensile deformation and shear deformation are summarized and compared below:

	Tensile (Figure 3.1a)	Shear (Figure 3.1c)
Stress	$\sigma = F/A$	$\tau = F/A$
Strain	$\varepsilon = (\ell - \ell_0)/\ell$	$\gamma = \tan \alpha$
Modulus	$E = \sigma/\varepsilon$	$G = \tau/\gamma$
Compliance	$D = \varepsilon/\sigma$	$J = \gamma/\tau$

It may be noted that for an ideal elastic body compliance is the inverse of modulus.

The modulus of elasticity, E , and the modulus of rigidity, G , as defined above, apply under longitudinal and shear forces, respectively. When a hydrostatic force is applied, a third elastic modulus, the modulus of compressibility or bulk modulus, K , is used. It is the reciprocal of compressibility, β , and is defined as the ratio of the hydrostatic pressure, σ_h , to the volumetric strain, $\Delta V/V_0$:

$$K = \frac{\sigma_h}{\Delta V/V_0} = \frac{1}{\beta} \quad (3.8)$$

As indicated in Figure 3.1, an elongation (or compression) in one direction, due to an axial force, produces a contraction (or expansion) in the lateral direction, i.e., at right angles to the direction of the force. The ratio of the lateral strain to the longitudinal strain is called Poisson's ratio ν . It is an important elastic constant. For instance, a tensile stress, σ_x , which produces a tensile strain, ε_x in the x -direction will also produce a contractive strain, ε_y , in the y -direction, the two being related by

$$\nu = -\varepsilon_y/\varepsilon_x \quad (3.9)$$

Combining Equation 3.9 with Equation 3.6 and rearranging yields

$$\varepsilon_y = -(\nu/E)\sigma_x \quad (3.10)$$

Equation 3.10 thus defines the contribution (ϵ_y) of the stress σ_x in the x -direction to the total strain in the y -direction.

Poisson's ratio, ν , as defined above, is a fourth elastic constant. For small deformations, the bulk modulus and modulus of rigidity can be calculated from the modulus of elasticity and Poisson's ratio by the following equations:

$$K = \frac{E}{3(1 - 2\nu)} \quad (3.11)$$

$$G = \frac{E}{2(1 + \nu)} \quad (3.12)$$

The elastic modulus can also be calculated from the bulk modulus and the modulus of rigidity by the relation

$$\frac{1}{E} = \frac{1}{9K} + \frac{1}{3G} \quad (3.13)$$

For soft materials such as gels, pastes, putties and many colloidal systems, which do not compress to the extent to which they are deformed under stress, K is very large compared to G , and therefore from Equation 3.13, $E = 3G$. For other materials as metals, fibers, and some plastics, however, K must be considered.

3.2.2 Stress–Strain Behavior

The stress–strain behavior of plastics measured at a constant rate of loading provides a basis for quality control and comparative evaluation of various plastics. The diagram shown in Figure 3.2a is most typical of that obtained in tension for a constant rate of loading. For compression and shear the behavior is quite similar except that the magnitude and the extent to which the curve is followed are different.

In the diagram, load per unit cross section (stress) is plotted against deformation expressed as a fraction of the original dimension (strain). Even for different materials the nature of the curves will be similar, but they will differ in (1) the numerical values obtained and (2) how far the course of the typical curve is followed before failure occurs. Cellulose acetate and many other thermoplastics may follow the typical curve for almost its entire course. Thermosets like phenolics, on the other hand, have cross-linked molecules, and only a limited amount of intermolecular slippage can occur. As a result, they undergo fracture at low strains, and the stress–strain curve is followed no further than to some point below the knee, such as point 1.

Ultimate strength, elongation, and elastic modulus (Young's modulus) can be obtained from the stress–strain study (Figure 3.2a). For determining Young's modulus (E) the slope of the initial tangent, i.e., the steepest portion of the curve, is measured. Other moduli values are also used for plastics (see Figure 3.2b).

The appearance of a permanent set is said to mark a yield point, which indicates the upper limit of usefulness for any material. Unlike some metals, in particular, the ferrous alloys, the drop-of-beam effect and a sharp knee in the stress–strain diagram are not exhibited by plastics. An arbitrary yield point is usually assigned to them. Typical of these arbitrary values is the 0.2% or the 1% offset yield stress (Figure 3.3a).

Alternatively, a yield stress can be defined as that at which the ratio of total stress to total strain is some selected amount, say 50% or 70% of the elastic modulus (Figure 3.3b). In the first case the yield stress is conveniently located graphically by offsetting to the right the stated amount of 0.2% (or 1%) and drawing a line paralleling that drawn for the elastic modulus. The point at which this line intersects the observed stress–strain line defined the yield stress. In the second case also the point of intersection of the line drawn with a slope of $0.7E$, for instance, with the observed stress–strain line determines the yield stress.

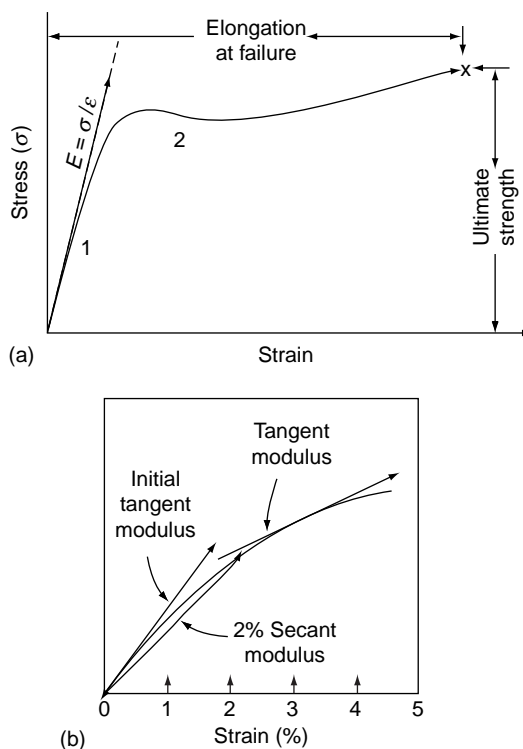


FIGURE 3.2 (a) Nominal stress–strain diagram. (b) Typical moduli values quoted for plastics.

Up to point 1 in Figure 3.2a, the material behaves as an elastic solid, and the deformation is recoverable. This deformation, which is small, is associated with the bending or stretching of the interatomic bonds between atoms of the polymer molecules (see Figure 3.4a). This type of deformation is nearly instantaneous and recoverable. There is no permanent displacement of the molecules relative to each other.

Between points 1 and 2 in Figure 3.2a, deformations have been associated with a straightening out of a kinked or coiled portion of the molecular chains (see Figure 3.4b), if loaded in tension. (For compression the reverse is true.) This can occur without intermolecular slippage. The deformation is recoverable ultimately but not instantaneously and hence is analogous to that of a nonlinear spring. Although the deformation occurs at stresses exceeding the stress at the proportional limit, there is no permanent change in intermolecular arrangement. This kind of deformation, characterized by recoverability and nonlinearity, is very pronounced in the rubber state.

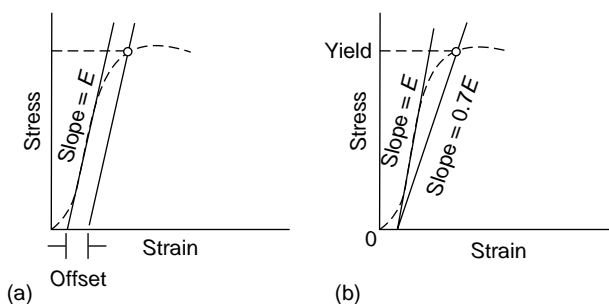


FIGURE 3.3 Location of a yield value.

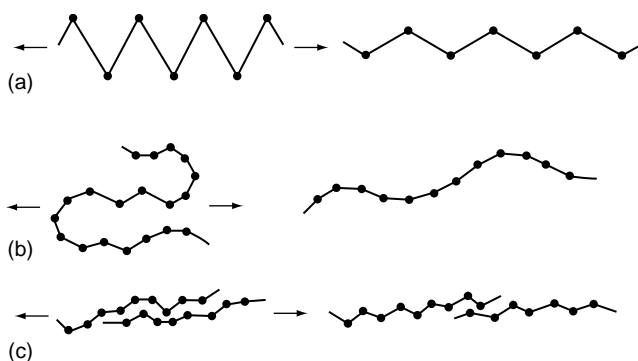


FIGURE 3.4 Deformation in plastics. (a) Stretching of polymer molecule. (b) Staightening out of a coiled molecular chain. (c) Intermolecular slippage.

The greatest extension that is recoverable marks the elastic limit for the material. Beyond this point extensions occur by displacement of molecules with respect to each other (Figure 3.4c), as in Newtonian flow of a liquid. The displaced molecules have no tendency to slip back to their original positions, therefore these deformations are permanent and not recoverable.

Poisson's ratio is a measure of the reduction in the cross section accompanying stretching and is the ratio of the transverse strain (a contraction for tensile stress) to longitudinal strain (elongation). Poisson's ratio for many of the more brittle plastics such as polystyrene, the acrylics, and the thermoset materials is about 0.3; for the more flexible plasticized materials, such as cellulose acetate, the value is somewhat higher, about 0.45. Poisson's ratio for rubber is 0.5 (characteristic of a liquid); it decrease to 0.4 for vulcanized rubber and to about 0.3 for ebonite. Poisson's ratio varies not only with the nature of the material but also with the magnitude of the strain for a given material. All values cited here are for zero strain.

Strain energy per unit volume is represented as the area under the stress–strain curve. It is another property that measures the ability of a material to withstand rough treatment and is related to toughness of the material. The stress-strain diagram thus serves as a basis for classification of plastics. Strong materials have higher ultimate strength than weak materials. Hard or unyielding materials have a higher modulus of elasticity (steeper initial slope) than soft materials. Tough materials have high elongations with large strain energy per unit volume. Stress–strain curves for type cases are shown in Figure 3.5.

It must be emphasized that the type behavior shown in Figure 3.5 depends not only on the material but also very definitely on conditions under which the test is made. For example, the bouncing putty silicone is putty-like under slow rates of loading (type curve a) but behaves as an elastic solid under high rates of impact (type curve b or d).

Figure 3.6a shows that at high extension rates (> 1 mm/sec) unplasticized PVC is almost brittle with a relatively high modulus and strength. At low extension rates (< 0.05 mm/sec) the same material exhibits a lower modulus and a high ductility, because at low extension rates the polymer molecular chains

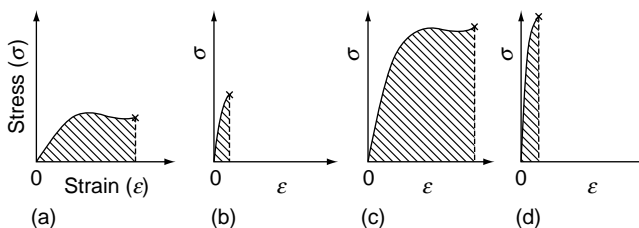


FIGURE 3.5 Classification of plastics on the basis of stress–strain diagram. (a) Soft and weak. (b) Weak and brittle. (c) Strong and tough. (d) Hard and strong.

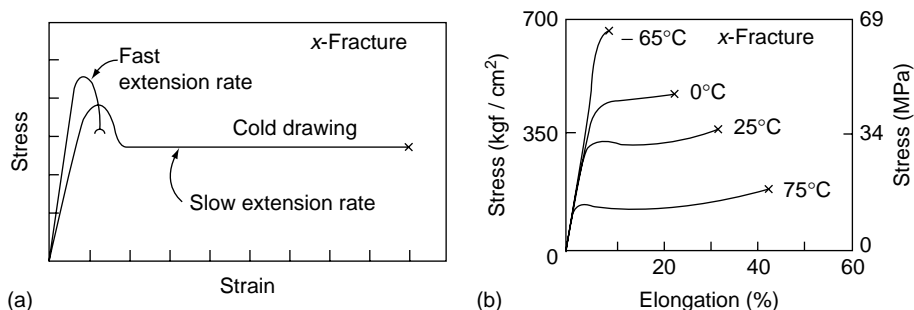


FIGURE 3.6 (a) Typical tensile behavior of unplasticized PVC. (b) Stress-strain curves of cellulose acetate at different temperatures.

have time to align themselves under the influence of the applied load. Thus the material is able to flow at the same rate as it is being strained. (This interesting phenomenon observed in some plastics is known as cold drawing.)

Further examples of the effect of conditions on the behavior of plastics are illustrated by the stress-strain curves for plasticized cellulose acetate when determined at different temperatures (Figure 3.6b). Thus the material is hard and strong at low temperatures, relatively tough at ordinary temperatures, and soft and weak at higher temperatures. This behavior may be attributed to variable molecular slippage effects associated with plasticizer action.

3.2.3 Viscoelastic Behavior of Plastics

In a perfectly elastic (Hookean) material the stress, σ , is directly proportional to the strain, ϵ . For uniaxial stress and strain the relationship may be written as

$$\sigma = \text{constant} \times \epsilon \quad (3.14)$$

where the constant is referred to as the modulus of elasticity.

In a perfectly viscous (Newtonian) liquid the shear stress, τ , is directly proportional to the rate of strain, $\dot{\gamma}$, and the relationship may be written as

$$\tau = \text{constant} \times \dot{\gamma} \quad (3.15)$$

where the constant is referred to as the viscosity.

Polymeric materials exhibit stress-strain behavior which falls somewhere between these two ideal cases; hence, they are termed viscoelastic. In a viscoelastic material the stress is a function of both strain and time and so may be described by an equation of the form

$$\sigma = f(\epsilon, t) \quad (3.16)$$

This equation represents nonlinear viscoelastic behavior. For simplicity of analysis it is often reduced to the form

$$\sigma = \epsilon f(t) \quad (3.17)$$

which represents linear viscoelasticity. It means that in a tensile test on linear viscoelastic material, for a fixed value of elapsed time, the stress will be directly proportional to strain.

The most characteristics features of viscoelastic materials are that they exhibit time-dependent deformation or strain when subjected to a constant stress (creep) and a time-dependent stress when

subjected to a constant strain (relaxation). Viscoelastic materials also have the ability to recover when the applied stress is removed. To a first approximation, this recovery can be considered as a reversal of creep.

3.2.3.1 Modulus and Compliance

Consider the tensile experiment of Figure 3.1a as a stress relaxation study in which the deformation is imposed suddenly and held fixed while the resulting stress, $\sigma(t)$, is followed with time. The tensile relaxation modulus, $E(t)$, is then obtained as

$$E(t) = \sigma(t)/\varepsilon_0 \quad (3.18)$$

with ε_0 being the constant strain and the parenthesis showing the functional dependence. Similarly a shear relaxation experiment measures the *shear* relaxation modulus $G(t)$:

$$G(t) = \tau(t)/\gamma_0 \quad (3.19)$$

where γ_0 is the constant strain.

Consider now the tensile experiment of Figure 3.1a as a creep study in which a steady stress σ_0 is suddenly applied to the polymer specimen and held constant. In general, the resulting strain $\varepsilon(t)$ will be a function of time starting from the imposition of load. The results of creep experiments are often expressed in terms of compliances rather than moduli. The tensile creep compliance $D(t)$ is

$$D(t) = \varepsilon(t)/\sigma_0 \quad (3.20)$$

The shear creep compliance $J(t)$ is similarly defined as

$$J(t) = \gamma(t)/\tau_0 \quad (3.21)$$

where τ_0 is the constant shear stress and $\gamma(t)$ is the resulting time-dependent strain.

A compliance is the inverse of a modulus for an ideal elastic body, but this is not true for viscoelastic materials. Consider, for example, two experiments carried out with identical samples of a viscoelastic material. In experiment (a) the sample is subjected to a tensile stress σ_1 for time t . The resulting tensile strain at t is ε_1 , and the creep compliance measured at that time is $D_1(t) = \varepsilon_1/\sigma_1$. In experiment (b) a sample is stressed to a level σ_2 such that strain ε_1 is achieved immediately. The stress is then gradually decreased so that the strain remains at ε_1 for time t (i.e., the sample does not creep further). Let the stress on the material at time t be σ_3 ; the corresponding relaxation modulus will be $E_2(t) = \sigma_3/\varepsilon_1$. In measurements of this type, it can be expected that $\sigma_2 > \sigma_1 > \sigma_3$ and $E(t) \neq 1/D(t)$.

$E(t)$ and $G(t)$ are obtained directly only from stress relaxation measurements, while $D(t)$ and $J(t)$ require creep experiments for their direct observation.

3.2.4 Stress–Strain–Time Behavior

When a mass of polymer is stressed the deformation produced may be considered as a sum of the following three deformations (see Figure 3.4):

1. A deformation due to bond bending and stretching which is instantaneous and independent of temperature (ordinary elastic deformation, ε_{oe}).
2. A deformation due to chain uncoiling which is not instantaneous and whose rate depends on temperature (high elastic deformation, ε_{he}).
3. A deformation due to slippage of polymer molecules past one another (viscous deformation ε_v). It is often assumed that the rates of such viscous deformation do not change with time if the applied stress is constant.

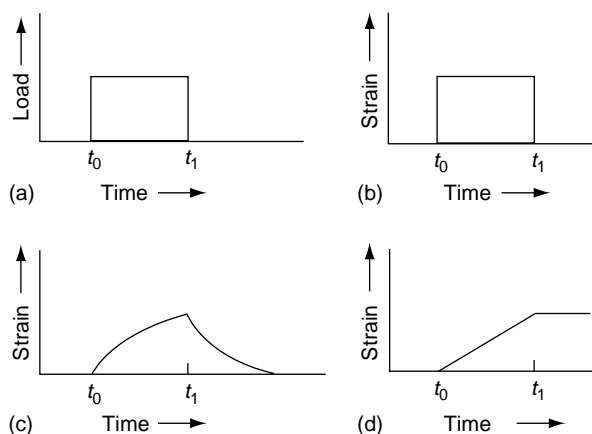


FIGURE 3.7 Types of deformational response as a result of (a) a fixed load being imposed between times t_0 and t_1 : (b) ordinary elastic material; (c) highly elastic material; (d) viscous material.

Figure 3.7 shows schematically the above types of deformational response as a result of a fixed stress imposed on a body showing ordinary elastic deformation only (Figure 3.7b), a second body showing high elastic deformation only (Figure 3.7c), and a third body showing viscous deformation only (Figure 3.7d). In each case, the stress is imposed at time t_0 and held at a constant value until time t_1 , when it is removed. Real polymers exhibit deformation-time curves which are a combination of the three basic responses, and a simple relationship for a combined or total strain ε

$$\varepsilon = \varepsilon_{oe} + \varepsilon_{he} + \varepsilon_v$$

can be used to analyze the deformation under a given stress.

The combined response, however, differs widely among polymers. Figure 3.8 shows typical deformation-time curves. It will be noted that, given sufficient time, ε_{he} will reach a constant value while ε_v continues to increase with time. On release of stress, ε_{he} will eventually disappear but ε_v will remain constant. An important conclusion resulting from this is that since both the high elastic and the viscous components of strain depend on both time and temperature the total strain also will depend on time and temperature. This has been shown to be an important factor affecting many polymer properties. It is therefore proposed to consider the background to this fact in greater detail in the following section.

3.2.4.1 The WLF Equations

For a polymeric segment to move from its position to its adjacent site there must be some holes in the mass of the material into which the segment can move—and simultaneously leave a vacant space into which another segment may move. The important point is that molecular motion cannot take place without the presence of holes. These holes, collectively, are called free volume.

One interpretation of the glass transition temperature (T_g) is that it is a temperature below which the free volume is really too small for much molecular movement. However, at or above T_g the molecules have sufficient energy for movement, jostling occurs and the free volume increases quite sharply with an increase in temperature.

It is usual to express the temperature coefficient of the free volume as being the difference between the thermal expansion coefficients above and below T_g . This may be expressed mathematically by the equation

$$f = f_g + (\alpha_a - \alpha_b)(T - T_g) = f_g + \Delta\alpha(T - T_g) \quad (3.22)$$

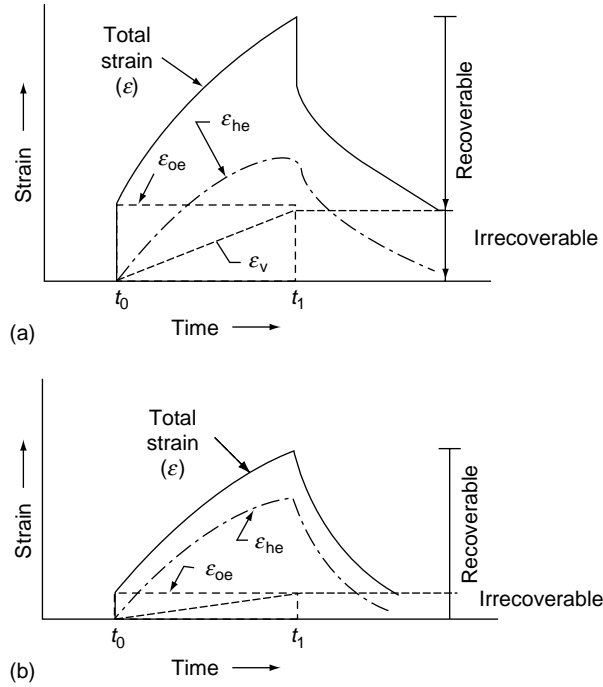


FIGURE 3.8 Strain-time curves: (a) material showing substantial ordinary elastic, high elastic, and viscous components of strain; (b) material in which high elastic deformation predominates.

where f is the fractional free volume at temperature T , f_g is the fractional free volume at T_g , and α_a and α_b are the coefficients of thermal expansion above and below the T_g , respectively. The value of $\Delta\alpha$ is simply ($\alpha_a - \alpha_b$).

Now it has been shown that the viscosity is related to the fractional free volume by an expression of the form

$$\frac{1}{\eta_T} = K e^{-A/f} \quad (3.23)$$

so that

$$\frac{1}{\eta_{T_R}} = K e^{-A/f_g} \quad (3.24)$$

where K and A are constants. Combining these one may write

$$\log_e \left(\frac{\eta_T}{\eta_{T_g}} \right) = \frac{1}{f} - \frac{1}{f_g} \quad (3.25)$$

Substituting for f from Equation 3.22, this expression yields

$$\log_{10} \left(\frac{\eta_T}{\eta_{T_g}} \right) = \frac{-(T - T_g)}{2.303 f_g [(f_g / \Delta\alpha) + (T - T_g)]} \quad (3.26)$$

Experimental data on a large range of polymers have demonstrated the approximate general validity of the equation

$$\log_{10} \left(\frac{\eta_T}{\eta_{T_g}} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (3.27)$$

known as the Williams, Landel, and Ferry Equation (WLF equation). Solving Equation 3.26 and Equation 3.27 one obtains $f_g = 0.025$ and $\Delta\alpha = 4.8 \times 10^{-4} \text{ deg}^{-1}$.

Equation 3.27 implies that if we know the viscosity at some temperature T we can estimate the viscosity at T_g , and from this estimate the viscosity at another temperature T_1 . The WLF equation thus gives the effect of temperature on viscosity.

There are also other applications of the WLF equation. In essence, if the value of material property changes with temperature, and if this change arises from changes in the viscosity of the system, then it may well be possible to apply the WLF equation to the property change.

One example of this is in relation to stress relaxation. If a polymer is deformed to a fixed strain at constant temperature, the force required to maintain that strain will decay with time due to viscous slippage of molecules. One measure of this rate of decay or stress relaxation is the relaxation time λ , which may be defined as the time taken for the stress to decrease to $1/e$ of its initial value on application of strain (discussed later). In this case, it is found that

$$\log_{10} \left(\frac{\lambda_T}{\lambda_{T_g}} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (3.28)$$

which is of the same form as Equation 3.27.

For experiments performed in shear, there is a rather complicated relation between the time-dependent stress relaxation shear modulus $G(t)$ defined by Equation 3.19 and the time-dependent creep compliance $J(t)$ defined by Equation 3.21. But if the slope of $\log G(t)$ versus $\log t$ is $-m$, then, to a good approximation,

$$G(t) \cdot J(t) = \frac{\sin m\pi}{m\pi} \quad (3.29)$$

for $m < 0.8$. Not only are $G(t)$ and $J(t)$ related, but the former in turn is related to the tensile modulus which itself is related to the stress relaxation time λ . It is therefore possible in theory to predict creep-temperature relationships from WLF data, though in practice these are best determined by experiments.

3.2.5 Creep Behavior

Except for a few exceptions like lead, metals generally exhibit creep at higher temperatures. Plastics and rubbers, however, possess very temperature-sensitive creep behavior; they exhibit significant creep even at room temperature. In creep tests a constant load or stress is applied to the material, and the variation of deformation or strain with time is recorded. A typical creep curve plotted from such a creep test is shown in Figure 3.9a. The Figure shows that there is typically an almost instantaneous elastic strain AB followed by a time-dependent strain, which occurs in three stages: primary or transient creep BC (stage I), secondary or steady-state creep CD (stage II), and tertiary or accelerated creep DE (stage III).

The primary creep has a rapidly decreasing strain rate. It is essentially similar in mechanism to retarded elasticity and, as such, is recoverable if the stress is removed. The secondary or steady-state creep is essentially viscous in character and is therefore nonrecoverable. The strain rate during this state is commonly referred to as the creep rate. It determines the useful life of the material. Tertiary

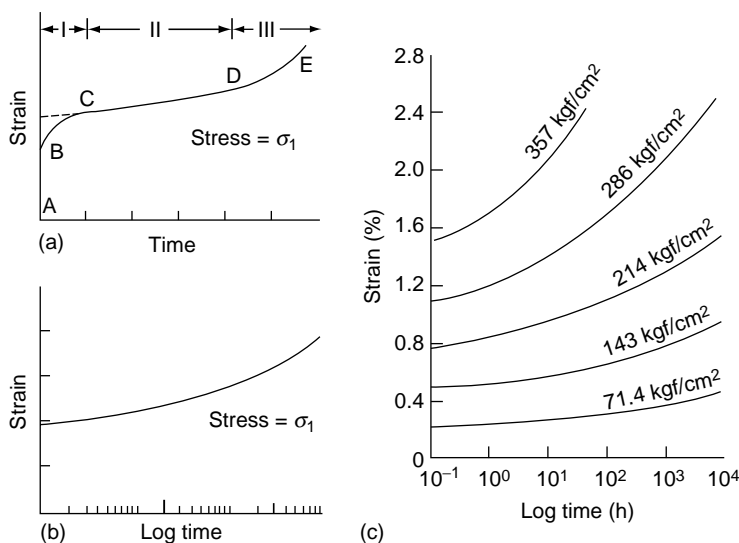


FIGURE 3.9 Typical creep curve (a) with linear time scale and (b) with logarithmic time scale. (c) Family of creep curves for poly(methyl methacrylate) at 20°C (1 kgf/cm² = 0.098 MPa).

creep occurs at an accelerated rate because of an increase in the true stress due to necking of the specimen.

Normally a logarithmic time scale is used to plot the creep curve, as shown in Figure 3.9b, so that the time dependence of strain after long periods can be included. If a material is linearly viscoelastic (Equation 3.17), then at any selected time each line in a family of creep curves (with equally spaced stress levels) should be offset along the strain axis by the same amount. Although this type of behavior may be observed for plastics at low strains and short times, in most cases the behavior is nonlinear, as indicated in Figure 3.9c.

Plastics generally exhibit high rates of creep under relatively low stresses and temperatures, which limits their use for structural purposes. Creep behavior varies widely from one polymer to another; thermoset polymers, in general, are much more creep resistant than thermoplastic polymers. The steady-state creep in plastics and rubbers (often referred to as cold flow) is due to viscous flow, and increases continuously. Clearly, the material cannot continue to get larger indefinitely, and eventually fracture will occur. This behavior is referred to as creep rupture. Creep strength of these materials is defined as the maximum stress which may be applied for a specified time without causing fracture. The creep strength of plastics is considerably increased by adding fillers and other reinforcing materials, such as glass fibers and glass cloth, since they reduce the rate of flow.

The creep and recovery of plastics can be simulated by an appropriate combination of elementary mechanical models for ideal elastic and ideal viscous deformations. Although there are no discrete molecular structures which behave like individual elements of the models, they nevertheless aid in understanding the response of plastic materials.

3.2.6 Maxwell Model

The Maxwell model consists of a spring and dashpot connected in series (Figure 3.10a). When a load is applied, the elastic displacement of the spring occurs immediately and is followed by the viscous flow of liquid in the dashpot which requires time. After the load is removed, the elastic displacement is recovered immediately, but the viscous displacement is not recovered.

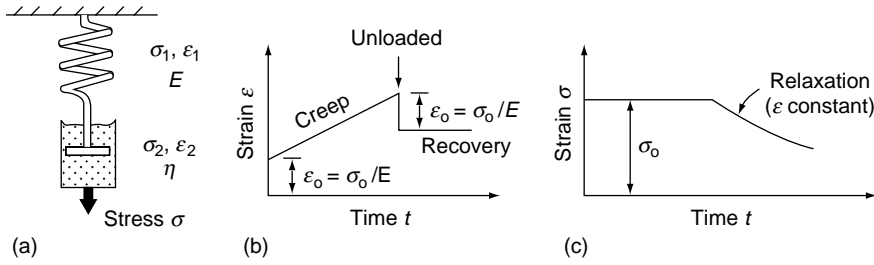


FIGURE 3.10 (a) The Maxwell model. (b), (c) Responses of the model under time-dependent modes of deformation.

3.2.6.1 Stress–Strain Relation

The spring is the elastic component of the response and obeys the relation

$$\sigma_1 = E\epsilon_1 \quad (3.30)$$

σ_1 and ϵ_1 are the stress and strain, respectively, and E is a constant.

The dashpot (consisting of a piston loosely fitting in a cylindrical vessel containing a liquid) accounts for the viscous component of the response. In this case the stress σ_2 , is proportional to the rate of strain $\dot{\epsilon}_2$; i.e.,

$$\sigma_2 = \eta\dot{\epsilon}_2 \quad (3.31)$$

where η is a material constant called the coefficient of viscous traction.

The total strain, ϵ , of the model under a given stress, σ , is distributed between the spring and the dashpot elements:

$$\epsilon = \epsilon_1 + \epsilon_2 \quad (3.32)$$

From Equation 3.32 the rate of total displacement with time is

$$\dot{\epsilon} = \dot{\epsilon}_1 + \dot{\epsilon}_2 \quad (3.33)$$

and from Equation 3.30 through Equation 3.32,

$$\dot{\epsilon} = \frac{1}{E}\dot{\sigma}_1 + \frac{1}{\eta}\sigma_2 \quad (3.34)$$

But both elements are subjected to the entire stress, σ ,

$$\sigma = \sigma_1 = \sigma_2 \quad (3.35)$$

Therefore Equation 3.34 can be written as

$$\dot{\epsilon} = \frac{1}{E}\dot{\sigma} + \frac{1}{\eta}\sigma \quad (3.36)$$

which is the governing equation of the Maxwell model. It is interesting to consider the responses that this model predicts under three common time-dependent modes of deformation.

Equation 3.36 is commonly rearranged as follows:

$$\dot{\sigma} = E\dot{\varepsilon} - \frac{1}{\lambda}\sigma \quad (3.37)$$

where $\lambda = \eta/E$ is the ratio of the viscosity η of the dashpot and the tensile modulus E of the spring.

Note that λ has the units of time and that it characterizes the viscoelastic nature of the element very concisely, as the ratio of the viscous portion of the response to the elastic portion. This naturally occurring parameter is taken to be the response time or the relaxation time of the model.

Equation 3.37 is the governing equation of the Maxwell model. It is interesting to consider the responses that this model predicts under three common time-dependent modes of deformation.

1. *Creep*. If a constant stress σ_0 is applied, then Equation 3.37 becomes

$$\dot{\varepsilon} = \frac{\sigma_0}{E} \frac{1}{\lambda} = \frac{\varepsilon_0}{\lambda} \quad (3.38)$$

Integration yields

$$\varepsilon = \varepsilon_0(1 + t/\lambda) \quad (3.39)$$

which indicates a constant rate of increase of strain with time—i.e., steady-state creep (Figure 3.10b). Equation 3.39 describes the creep response of the Maxwell element.

2. *Relaxation*. If the strain is held constant, then Equation 3.37 becomes

$$\dot{\sigma} + \sigma/\lambda = 0 \quad (3.40)$$

Solving this differential equation with the initial condition $\sigma = \sigma_0$ at $t = t_0$ gives

$$\sigma = \sigma_0 \exp(-t/\lambda) \quad (3.41)$$

This indicates an exponential decay of stress with time (Figure 3.10c). The stress will relax and approach zero monotonically. The relaxation time λ is thus the time required for the stress to decay to $1/e$, or 0.37, of its initial value.

Since the strain remains constant in a relaxation experiment, Equation 3.41 can also be written as

$$E(t) = E_0 \exp(-t/\lambda) \quad (3.42)$$

where $E(t)$ is the tensile modulus of the Maxwell element at time t , and E_0 the modulus at the initial time of deformation.

The corresponding equation for the Maxwell element in shear is

$$G(t) = G_0 \exp(-t/\lambda) \quad (3.43)$$

where $G(t)$ is the shear modulus of the Maxwell element at time t , and G_0 is the modulus at $t = 0$; the relaxation time λ is now the ratio of the viscosity η of the viscous component and the shear modulus G of the elastic component of the model.

3. *Recovery*. When the initial stress, σ_0 , is removed, there is an instantaneous recovery of the elastic strain, ε_0 , and then, as shown by Equation 3.36, the strain rate is zero, so there is no further recovery (Figure 3.10b).

3.2.6.2 Generalized Maxwell Model

The behavior of a polymer system is so complicated that we cannot represent it with the response time of a single Maxwell element. In other words, the simple model described above cannot approach the behavior of a real system. In 1893, Weichert showed that stress-relaxation experiments could be represented as a generalization of Maxwell's equation. The mechanical model according to Weichert's formulation is shown in Figure 3.11; it consists of a large number of Maxwell elements coupled in parallel.

Since the strain in each element is common, we sum the forces acting on the individual elements to obtain the total stress as a function of time, i.e.,

$$\sigma(t) = \sum \sigma_i \quad (3.44)$$

For relaxation with constant strain ε_0 we combine Equation 3.41 and Equation 3.44 to obtain

$$\sigma(t) = \varepsilon_0 \sum E_i \exp\left(-\frac{t}{\lambda_i}\right) \quad (3.45)$$

where $\lambda_i = \eta_i/E_i$ is the relaxation time of the i th element.

The overall modulus as a function of time, $E(t)$, is thus

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} = \sum E_i \exp\left(-\frac{t}{\lambda_i}\right) \quad (3.46)$$

The synthesis of $E(t)$ from known values of E_i and λ_i is simplified by the use of semilog paper.

Example 3.1

Derive the overall time-dependent modulus $E(t)$ for $0 < t < 200$ sec when

i	E_0 [(dynes/cm ²) $\times 10^{-8}$]	λ_i (sec)
1	1.000	100
2	0.667	50
3	0.333	25

Answer. For each element, $E_i(t)$ is given by a straight line on semilog paper (Equation 3.42) with intercept $(E_i)_0$ and a negative slope of λ_i (Figure 3.12). Adding the curves arithmetically gives $E(t)$ directly:

$$E_i(t) = (E_i)_0 \exp\left(-\frac{t}{\lambda_i}\right)$$

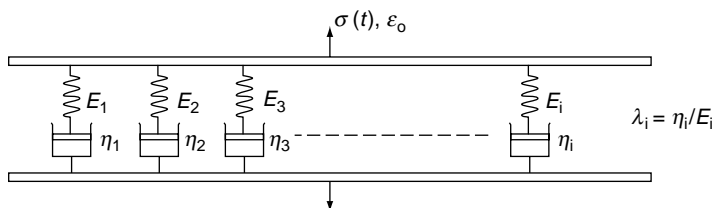


FIGURE 3.11 Generalized Maxwell model (Weichert's formulation).

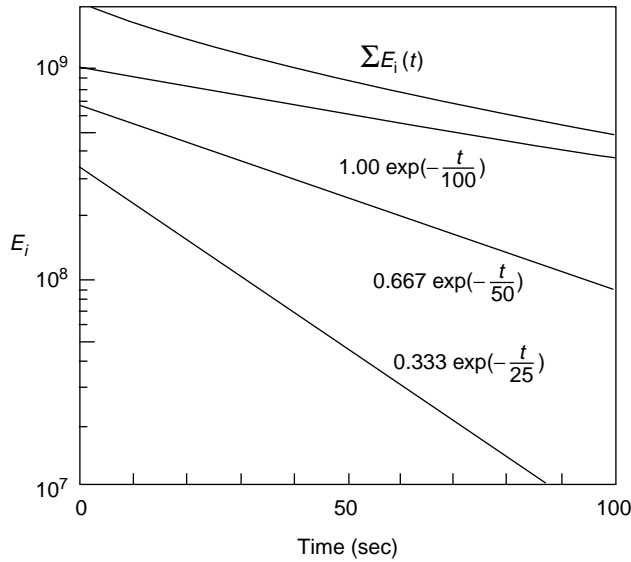


FIGURE 3.12 Time-dependent modulus for individual Maxwell elements and for the sum of three elements in parallel $\sum E_i(t)$.

$$E(t) = \sum_{i=1}^3 E_i(t)$$

Note that $E(t)$ is not a straight line in Figure 3.12.

As can be seen, the Maxwell–Weichert model possesses many relaxation times. For real materials we postulate the existence of a continuous spectrum of relaxation times (λ_i). A spectrum-skewed toward lower times would be characteristic of a viscoelastic fluid, whereas a spectrum skewed toward longer times would be characteristic of a viscoelastic solid. For a real system containing crosslinks the spectrum would be skewed heavily toward very long or infinite relaxation times. In generalizing, λ may thus be allowed to range from zero to infinity. The concept that a continuous distribution of relaxation times should be required to represent the behavior of real systems would seem to follow naturally from the fact that real polymeric systems also exhibit distributions in conformational size, molecular weight, and distance between crosslinks.

If the number of units is allowed to become infinite, the summation over the differential units of the model (Equation 3.44) can be explained by an integration over all relaxation times. Thus as $i \rightarrow \infty$ in Figure 3.11, the range of allowable relaxation times becomes zero to infinity. From the notion that the stresses in the individual elements, σ_i , are functions of time and relaxation times, $\sigma_i = \sigma_i(t, \lambda_i)$, we define a continuous function $\sigma(t, \lambda)$ such that the total stress, $\sigma(t)$, is given by the following [compare Equation 3.44]:

$$\sigma(t) = \int_0^{\infty} \sigma(t, \lambda) d\lambda \quad (3.47)$$

and for relaxation with constant strain, ε_0 , it is given by the following (compare Equation 3.45):

$$\sigma(t) = \varepsilon_0 \int_0^{\infty} E(\lambda) e^{-t/\lambda} d\lambda \quad (3.48)$$

Since $E(t) = \sigma(t)/\varepsilon_0$, we find that we have developed an expression suitable for representing the time dependence of the relaxation modulus, i.e.,

$$E(t) = \int_0^{\infty} E(\lambda) e^{-t/\lambda} d\lambda \quad (3.49)$$

The function $E(\lambda)$ is referred to as the distribution of relaxation times or the relaxation spectrum. In principle, once $E(\lambda)$ is known, the result of any other type of mechanical experiment can be predicted. In practice $E(\lambda)$ is determined from experimental data on $E(t)$. Since the distribution of relaxation times is so broad, it is more convenient to consider $\ln \lambda$. Hence we introduce the function $H(\ln \lambda)$, where the parenthesis denotes functional dependence, to replace $E(\lambda)$ as

$$E(\lambda) = \frac{H(\ln \lambda)}{\lambda} \quad (3.50)$$

Then Equation 3.49 becomes (note the change of limits):

$$E(t) = \int_{-\infty}^{+\infty} H(\ln \lambda) e^{-t/\lambda} d(\ln \lambda) \quad (3.51)$$

and all relaxation times are considered as $\ln \lambda$.

What we desire now is a means to determine $H(\ln \lambda)$ from data obtained as $E(t)$ versus $\ln t$. This is virtually impossible to do directly, and a number of approximate methods have been devised. These approximation are discussed in the advanced reference works of Ferry [5] and Tobolsky [6].

3.2.7 Kelvin or Voigt Model

In the Kelvin or Voigt model the spring and dashpot elements are connected in parallel, as shown in Figure 3.13a. This model roughly approximates the behavior of rubber. When the load is applied at zero time, the elastic deformation cannot occur immediately because the rate of flow is limited by the dashpot. Displacements continue until the strain equals the elastic deformation of the spring and it resists further movement. On removal of the load the spring recovers the displacement by reversing the

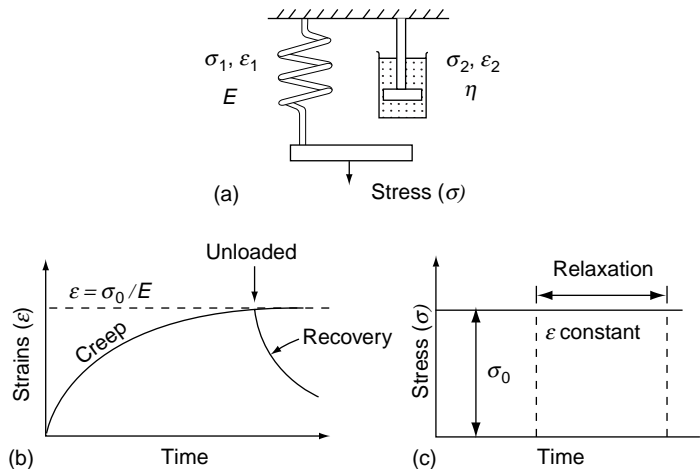


FIGURE 3.13 (a) The Kelvin or Voigt model. (b), (c) Responses of the model under time-dependent modes of deformation.

flow through the dashpot, and ultimately there is no strain. The mathematical relations are derived next.

3.2.7.1 Stress–Strain Relation

Since the two elements are connected in parallel, the total stress will be distributed between them, but any deformation will take place equally and simultaneously in both of them; that is,

$$\sigma = \sigma_1 + \sigma_2 \quad (3.52)$$

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \quad (3.53)$$

From Equation 3.30, Equation 3.31, and Equation 3.52,

$$\sigma = E\varepsilon_1 + \eta\dot{\varepsilon}_2$$

or, using Equation 3.53,

$$\sigma = E\varepsilon + \eta\dot{\varepsilon} \quad (3.54)$$

which is the governing equation for the Kelvin (or Voigt) model. Its predictions for the common time-dependent deformations are derived next.

1. *Creep*. If a constant stress, σ_0 , is applied, Equation 3.54 becomes

$$\sigma_0 = E\varepsilon + \eta\dot{\varepsilon} \quad (3.55)$$

The differential equation may be solved for the total strain, ε , to give

$$\varepsilon = \frac{\sigma_0}{E} \left[1 - \exp\left(-\frac{E}{\eta}t\right) \right] \quad (3.56)$$

This equation indicates that the deformation does not appear instantaneously on application of stress, but it increases gradually, attaining asymptotically its maximum value $\varepsilon = \sigma_0/E$ at infinite time (Figure 3.13b). The Voigt model is thus said to exhibit retarded elastic deformation in creep experiments. The quantity $\eta/E = \lambda$ is called a retardation time. It is the time ($t = \lambda$) at which the deformation is retarded by $1/e$ of its maximum value. (The physical meaning of η/E for Maxwell and Voigt models should not be confused.)

By comparison with Equation 3.56 the creep equation under a constant shear stress τ_0 may be written as

$$\gamma = \frac{\tau_0}{G} [1 - \exp(-t/\lambda)] \quad (3.57)$$

where γ is the time-dependent shear strain of the Voigt element and G is the shear modulus of its elastic component; λ is the retardation time ($= \eta/G$).

Equation 3.57 is conveniently written as

$$J = J_0 [1 - \exp(-t/\lambda)] \quad (3.58)$$

where J is the shear creep compliance ($= \gamma/\tau_0$) at time t , and J_0 is the shear creep compliance at the time of stress application.

2. *Relaxation*. If the strain is held constant; then Equation 3.54 becomes:

$$\sigma = E\varepsilon$$

3. *Recovery*. If the stress is removed, Equation 3.54 becomes

$$0 = E\varepsilon + \eta\dot{\varepsilon}$$

This differential equation may be solved with the initial condition $\varepsilon = \varepsilon_0$ at the time of stress removal to give

$$\varepsilon = \varepsilon_0 \exp\left(-\frac{E}{\eta}t\right) \quad (3.59)$$

This equation represents an exponential recovery of strain which, as a comparison with Equation 3.56 shows, is a reversal of the predicted creep.

The Kelvin (or Voigt) model therefore gives an acceptable first approximation to creep and recovery behavior but does not predict relaxation. By comparison, the previous model (Maxwell model) could account for relaxation but was poor in relation to creep and recovery. It is evident therefore that a better simulation of viscoelastic materials may be achieved by combining the two models.

3.2.8 Four-Element Model

A combination of the Maxwell and Kelvin models comprising four elements is shown in Figure 3.14a. The total strain is

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \dot{\varepsilon}_k \quad (3.60)$$

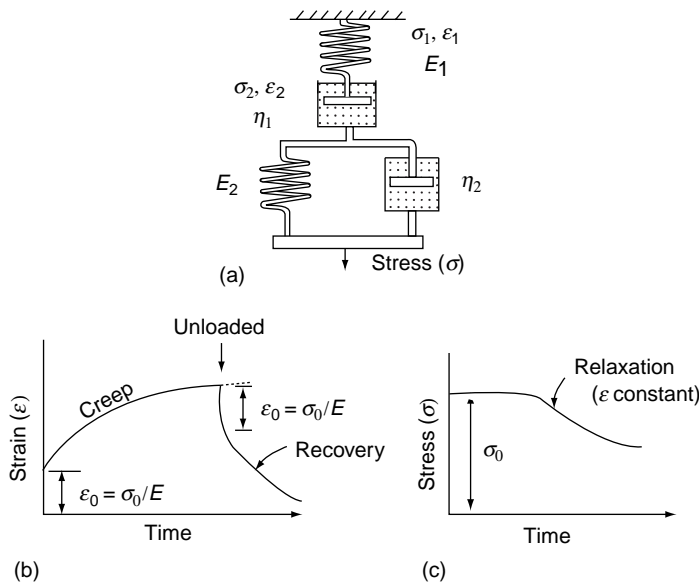


FIGURE 3.14 (a) Four-element model. (b), (c) Responses of the model under time-dependent modes of deformation.

where ε_k is the strain response of the Kelvin model. From Equation 3.30, Equation 3.31, and Equation 3.56,

$$\varepsilon = \frac{\sigma_0}{E_1} + \frac{\sigma_0 t}{\eta_1} + \frac{\sigma_0}{E_2} \left[1 - \exp\left(-\frac{E_2}{\eta_2} t\right) \right] \quad (3.61)$$

Thus the strain rate is

$$\dot{\varepsilon} = \frac{\sigma_0}{\eta_1} + \frac{\sigma_0}{\eta_2} \exp\left(-\frac{E_2}{\eta_2} t\right) \quad (3.62)$$

The response of this model to creep, relaxation, and recovery situations is thus the sum of the effects described previously for the Maxwell and Kelvin models and is illustrated in Figure 3.14b.

Though the model is not a true representation of the complex viscoelastic response of polymeric materials, it is nonetheless an acceptable approximation to the actual behavior. The simulation becomes better as more and more elements are added to the model, but the mathematics also becomes more complex.

3.2.9 Zener Model

Another model, attributed to Zener, consists of three elements connected in series and parallel, as illustrated in Figure 3.15, and known as the standard linear solid. Following the procedure already given, we derive the governing equation of this model:

$$\eta_3 \dot{\sigma} + E_1 \sigma = \eta_3 (E_1 + E_2) \dot{\varepsilon} + E_1 E_2 \varepsilon \quad (3.63)$$

This equation may be written in the form

$$a_1 \dot{\sigma} + a_0 \sigma = b_1 \dot{\varepsilon} + b_0 \varepsilon \quad (3.64)$$

where a_1 , a_0 , b_1 , and b_0 are all material constants. A more general form of Equation 3.64 is

$$\begin{aligned} a_n \frac{\partial^n \sigma}{\partial t^n} + a_{n-1} \frac{\partial^{n-1} \sigma}{\partial t^{n-1}} + \cdots + a_0 \sigma \\ = b_m \frac{\partial^m \varepsilon}{\partial t^m} + \cdots + b_0 \varepsilon \end{aligned} \quad (3.65)$$

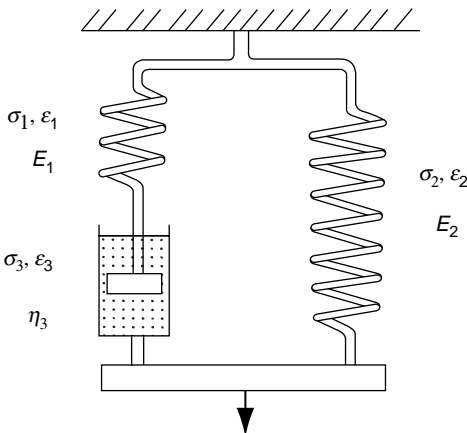


FIGURE 3.15 The standard linear solid.

The modern theory of viscoelasticity favors this type of equation. The models described earlier are special cases of this equation.

Hookean body. All constants a and b except a_0 and b_0 are zero. Equation 3.65 becomes

$$a_0 \sigma = b_0 \varepsilon \quad (3.65a)$$

Maxwell element. All constant a and b except a_0 , a_1 , and b_1 are zero. Equation 3.65 becomes

$$a_0 \sigma + a_1 \frac{\partial \sigma}{\partial t} = b_1 \frac{\partial \varepsilon}{\partial t} \quad (3.65b)$$

This is the spring and dashpot in series and applies to stress relaxation at constant strain. *Voigt element*. All constants a and b except a_0 , b_0 , and b_1 are zero. Equation 3.65 becomes

$$a_0\sigma = b_0\varepsilon + b_1\frac{\partial\varepsilon}{\partial t} \quad (3.65c)$$

This is the spring and dashpot in parallel and applies to strain retardation at constant stress.

3.2.10 Superposition Principle

Each of the creep curves in Figure 3.9c depicts the strain response of a material under a constant stress. However, in service, materials are often subjected to a complex sequence of stresses or stress histories, and obviously it is not practical to obtain experimental creep data for all combinations of loading. In such cases a theoretical model can be very useful for describing the response of a material to a given loading pattern.

The most commonly used model is the Boltzmann superposition principle, which proposes that for a linear viscoelastic material the entire loading history contributes to the strain response, and the latter is simply given by the algebraic sum of the strains due to each step in the load. The principle may be expressed as follows. If an equation for the strain is obtained as a function of time under a constant stress, then the modulus as a function of time may be expressed as

$$E(t) = \frac{\sigma}{\varepsilon(t)} \quad (3.66)$$

Thus if the applied stress is σ_0 at zero time, the creep strain at any time, t , will be given by

$$\varepsilon(t) = \frac{1}{E(t)}\sigma_0 \quad (3.67)$$

On the other hand, if the stress, σ_0 , was applied at zero time and an additional stress, σ_1 , at time u , the Boltzmann superposition principle says that the total strain at time t is the algebraic sum of two independent responses; that is,

$$\varepsilon(t) = \frac{1}{E(t)}\sigma_0 + \frac{1}{E(t-u)}\sigma_1 \quad (3.68)$$

For any series of stress increments this equation can be generalized to

$$\varepsilon(t) = \sum_{u=-\infty}^{u=t} \sigma_i \frac{1}{E(t-u)} \quad (3.69)$$

The lower limit of the summation is taken as $-\infty$ since the entire stress history contributes to the response.

As an illustration, for a series of step changes in stress as in Figure 3.16a, the strain response predicted by the model is shown schematically in Figure 3.16b. The time-dependent strain response (creep curve) due to the stress σ_0 applied at zero time is predicted by Equation 3.66 with $\sigma = \sigma_0$. When a second stress, σ_1 , is added to σ_0 , the new curve will be obtained, as illustrated in Figure 3.16b, by adding the creep due to σ_1 to the anticipated creep due to σ_0 . Removal of all stress at a subsequent time u_2 is then equivalent to removing the creep strain due to σ_0 and σ_1 , independently, as shown in Figure 3.16b. The procedure is repeated in a similar way for other stress changes.

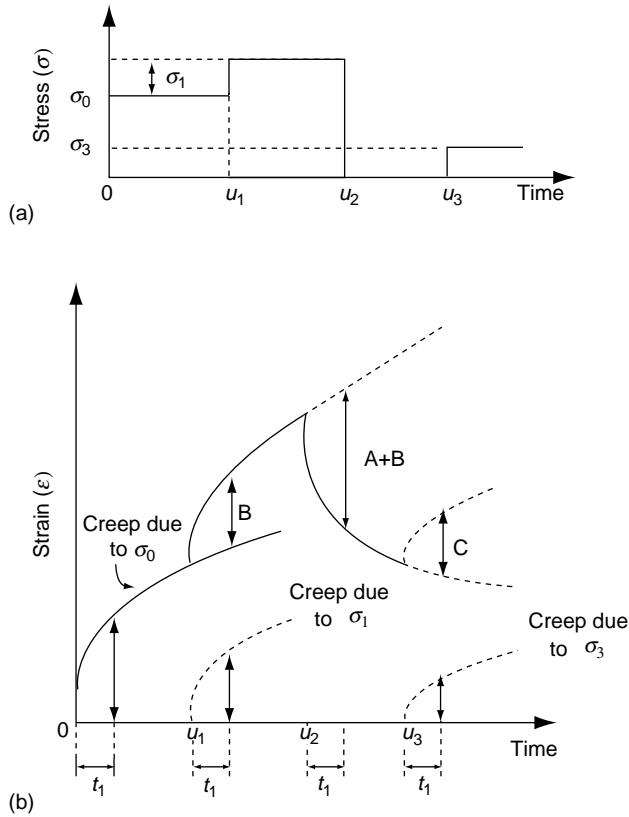


FIGURE 3.16 (a) Stress history. (b) Predicted Strain response using Boltzmann's superposition principle.

To take into account a continuous loading cycle, we can further generalize Equation 3.69 to

$$\epsilon(t) = \int_{-\infty}^t \frac{1}{E(t-u)} \frac{d\sigma(u)}{du} du \quad (3.70)$$

In the same way the stress response to a complex strain history may be derived as

$$\sigma(t) = \int_{-\infty}^t E(t-u) \frac{d\epsilon(u)}{du} du \quad (3.71)$$

When the stress history has been defined mathematically, substitution in Equation 3.70 and integration within limits gives the strain at the given time. The stress at a given time is similarly obtained from Equation 3.71.

3.2.11 Isometric and Isochronous Curves

Isometric curves are obtained by plotting stress vs. time for a constant strain; *isochronous curves* are obtained by plotting stress vs. strain for a constant time of loading. These curves may be obtained from the creep curves by taking a constant-strain section and a constant-time section, respectively, through the creep curves and replotting the data, as shown in [Figure 3.17](#).

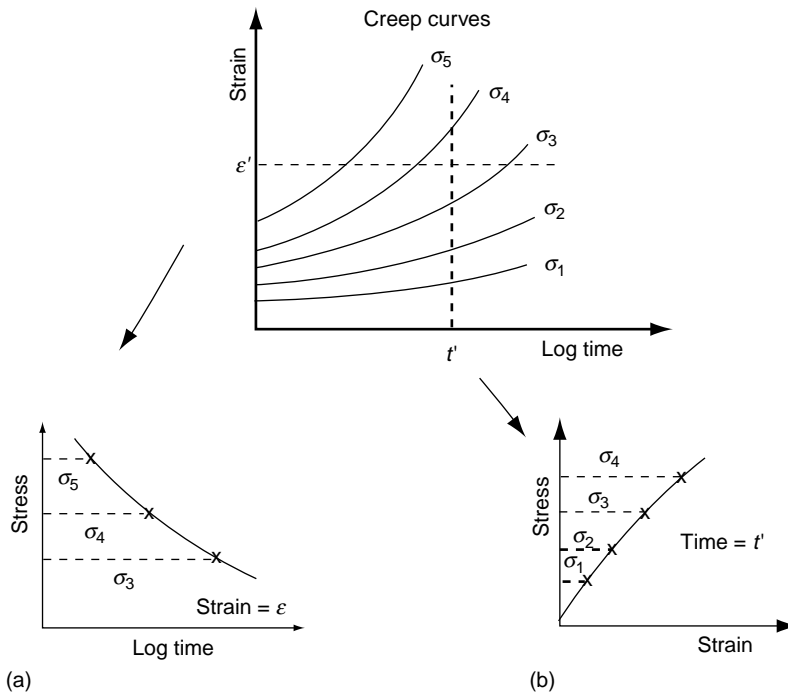


FIGURE 3.17 (a) Isometric and (b) isochronous curves from creep curves.

An isometric curve provides an indication of the relaxation of stress in the material when the strain is kept constant. Since stress relaxation is a less common experimental procedure than creep testing, an isometric curve, derived like the preceding curves from creep curves, is often used as a good approximation of this property.

Isochronous curves, on the other hand, are more advantageously obtained by direct experiments because they are less time consuming and require less specimen preparation than creep testing. The experiments actually involve a series of mini creep and recovery tests on the material. Thus a stress is applied to a specimen of the material, and the strain is recorded after a time t (typically 100 sec). The stress is then removed and the material is allowed to recover. This procedure is repeated until there are sufficient points to plot the isochronous curve.

Note that the isochronous test method is quite similar to that of a conventional incremental loading tensile test and differs only in that the presence of creep is recognized and the “memory” of the material for its stress history is overcome by the recovery periods. Isochronous data are often presented on log–log scales because this provides a more precise indication of the nonlinearity of the data by yielding a straight-line plot of slope less than unity.

3.2.12 Pseudoelastic Design Method

Due to the viscoelastic nature of plastics, deformations depend on such factors as the time under load and the temperature. Therefore the classical equations available for the design of structural components, such as springs, beams, plates, and cylinders, and derived under the assumptions that (1) the modulus is constant and (2) the strains are small and independent of loading rate or history and are immediately reversible, cannot be used indiscriminately. For example, classical equations are derived using the relation

$$\text{Stress} = \text{constant} \times \text{strain}$$

where the constant is the modulus. From the nature of the creep curves shown in Figure 3.17a, it is clear that the modulus of a plastic is not constant. Several approaches have been developed to allow for this fact, and some of them also give very accurate results; but mathematically they are quite complex, and this has limited their use. However, one method that has been widely accepted is the *pseudoelastic design method*. In this method appropriate values are chosen for the time-dependent properties, such as modulus, and substituted into the classical equations.

The method has been found to give sufficiently accurate results, provided that the value of the modulus is chosen judiciously, taking into account the service life of the component and the limiting strain of the plastic. Unfortunately, however, there is no straightforward method for finding the limiting strain of a plastic. The value may differ for various plastics and even for the same plastic in different applications. The value is often arbitrarily chosen, although several methods have been suggested for arriving at an appropriate value.

One method is to draw a secant modulus which is 0.85 of the initial tangent modulus and to note the strain at which this intersects the stress-strain curve (see Figure 3.2b). But this method may be too restrictive for many plastics, particularly those which are highly crystalline. In most situations the maximum allowable strain is therefore decided in consultations between designer and product manufacturer.

Once an appropriate value for the maximum strain is chosen, design methods based on creep curves and the classical equations are quite straightforward, as shown in the following examples.

Example 3.2

A plastic beam, 200 mm long and simply supported at each end, is subjected to a point load of 10 kg at its mid-span. If the width of the beam is 14 mm, calculate a suitable depth so that the central deflection does not exceed 5 mm in a service life of 20,000 h. The creep curves for the material at the service temperature of 20°C are shown in Figure 3.18a. The maximum permissible strain in this material is assumed to be 1%.

Answer. The linear elastic equation for the central deflection, δ , of the beam is

$$\delta = \frac{PL^3}{48EI}$$

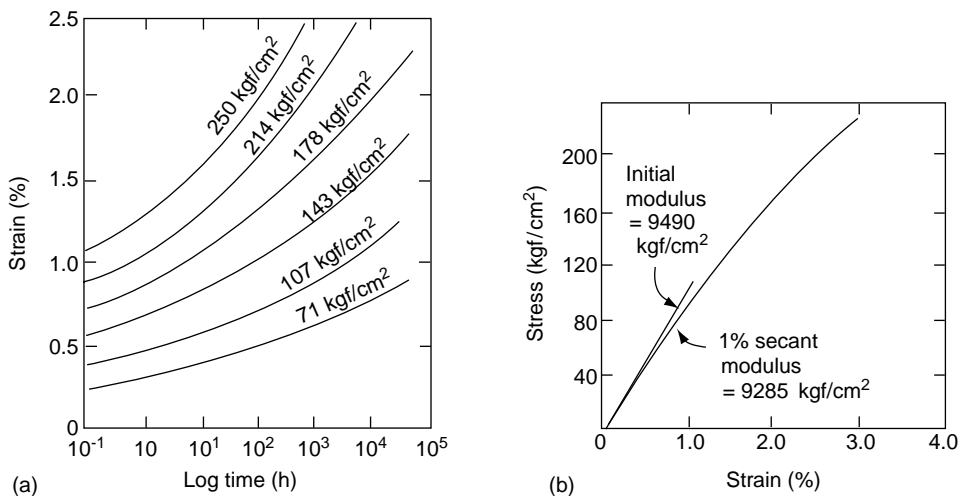


FIGURE 3.18 (a) Creep curves for material used in illustrative examples. (b) Isochronous curve at 20,000 h service life (1 kgf/cm² = 0.098 MPa).

where P , load at mid-span; L , length of beam; E , modulus of beam material; I , second moment of area of beam cross section

The second moment of area is

$$I = \frac{bd^3}{12} = \frac{14d^3}{12} \text{ mm}^4$$

So from the expression for δ ,

$$d^3 = \frac{PL^3}{56E\delta}$$

The only unknown on the right side is E . For plastic this is time dependent, but a suitable value corresponding to the maximum permissible strain may be obtained by referring to the creep curves in Figure 3.18a. A constant-time section across these curves at 20,000 h gives the isochronous curve shown in Figure 3.18b. Since the maximum strain is recommended as 1%, a secant modulus may be taken at this value. It is 9285 kgf/cm² (=92.85 kgf/mm²). Using this value in the above equation gives

$$d^3 = \frac{10(200)^3}{56 \times 92.85 \times 5}$$

$$d = 14.5 \text{ mm}$$

Example 3.3

A thin-wall plastic pipe of diameter 150 mm is subjected to an internal pressure of 8 kgf/cm² at 20°C. It is suggested that the service life of the pipe should be 20,000 h with a maximum strain of 2%. The creep curves for the plastic material are shown in Figure 3.18a. Calculate a suitable wall thickness for the pipe.

Answer. The hoop stress, σ , in a thin-wall pipe of diameter d and thickness h , subjected to an internal pressure, P , is given by

$$\sigma = \frac{Pd}{2h} \quad \text{so} \quad h = \frac{Pd}{2\sigma}$$

A suitable design stress may be obtained from the creep curves in Figure 3.18a. By referring to the 20,000-h isochronous curve (Figure 3.18b) derived from these curves, the design stress at 2% strain is obtained as 167.7 kg/cm². (Note that a similar result could have been obtained by plotting a 2% isometric curve from the creep curves and reading the design stress at a service life of 20,000 h.) Substituting the design stress into the equation for h gives

$$h = \frac{8 \times 150}{2 \times 167.7} = 3.58 \text{ mm}$$

It may be seen from the creep curves (Figure 3.18a) that when the pipe is first pressurized, the strain is less than 1%. Then as the material creeps, the strain increases steadily to reach its limit of 2% at 20,000 h.

In both examples it has been assumed that the service temperature is 20°C. If this is not the case, then creep curves at the appropriate temperature should be used. However, if none are available, a linear extrapolation between available temperatures may be sufficient for most purposes.

Again, for some materials like nylon the moisture content of the material has a significant effect on its creep behavior. In such a case creep curves are normally available for the material in both wet and dry states, and appropriate data should be used, depending on the service conditions.

3.2.13 Effect of Temperature

Many attempts have been made to obtain mathematical expressions which describe the time and temperature dependence of the strength of plastics. Since for many plastics at constant temperature a plot of stress, σ , against the logarithm of time to failure (creep rupture), t , is approximately linear, one of the expressions most commonly used is

$$t = Ae^{-B\sigma} \quad (3.72)$$

where A and B are constants. In reality, however, they depend on factors such as material structure and on temperature.

The most successful attempts to include the effects of temperature in a relatively simple expression have been made by Zhurkov and Bueche, who used an equation of the form [7]

$$t = t_0 \exp\left(\frac{U_0 - \gamma\sigma}{RT}\right) \quad (3.73)$$

where t_0 is a constant which has approximately the same value for most plastics, U_0 is the activation energy of the fracture process, γ is a coefficient which depends on the structure of the material, R is the molar gas constant, and T is the absolute temperature.

A series of creep rupture tests on a given material at a fixed temperature would permit the values for U_0 and γ for the material to be determined from this expression. The times to failure at other stresses and temperatures could then be predicted.

The relative effects of temperature rises on different plastic materials depend on the structure of each material and, particularly, whether it is crystalline or amorphous. If a plastic is largely amorphous (e.g., polymethyl methacrylate, polystyrene), then it is the glass transition temperature (T_g) which will determine the maximum service temperature, since above T_g the material passes into the rubbery region (see [Figure 1.19](#)).

On the other hand, in plastics which have a high degree of crystallinity (e.g., polyethylene, polypropylene), the amorphous regions are small, so T_g is only of secondary importance. For them it is the melting temperature which will limit the maximum service temperature. The lowest service temperatures which can be used are normally limited by the brittleness introduced into the material. The behavior of plastics materials at room temperature is related to their respective T_g values. This aspect has been dealt with in [Chapter 1](#).

3.2.14 Time–Temperature Superposition

In engineering practice, it is often necessary to design for the use of a material over a long period of time—many years, for example. A common parameter to use in design work is the elastic modulus. We know, however, that for polymers the modulus decreases with increasing time under load.

Accumulation of long-term data for design with plastics can be very inconvenient and expensive. A method is thus needed to extrapolate data from shorter time studies at higher temperature to longer times over several decades of time scale at the desired temperature so that a lower limit of the modulus can be determined for use in design. On the other hand, it is sometimes difficult to obtain data over a very short time scale. One must then extrapolate data obtained under practicable experimental conditions to these short time scales. An empirical method for such extrapolations is available for amorphous polymer systems and, in general, for polymer systems where structure does not change during the period of testing.

The aforesaid extrapolations make use of a time-temperature superposition principle which is based on the fact that time and temperature have essentially equivalent effects on the modulus values of amorphous polymers. [Figure 3.19](#) shows modulus data taken at several temperatures for poly(methyl methacrylate) [8]. Because of the equivalent effect of time and temperature, data at different

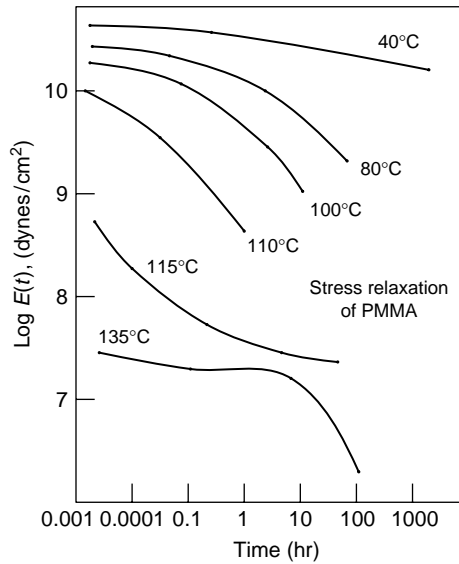


FIGURE 3.19 Logarithm of tensile relaxation modulus versus logarithm of time for unfractionated poly(methyl methacrylate) of $\bar{M}_v = 3.6 \times 10^6$. (After McLoughlin, J. R. and Tobolsky, A. V. 1952. *J. Colloid Sci.*, 7, 555.)

temperatures can be superposed on data taken at a specified reference temperature merely by shifting individual curves one at a time and consecutively along the log t axis about the reference temperature.

This time-temperature superposition procedure has the effect of producing a single continuous curve of modulus values extending over many decades of log t at the reference temperature. A curve constructed in this way, as shown in Figure 3.20 (with a reference temperature 115°C), is known as the master curve.

The time-temperature superposition can be expressed mathematically as

$$E(T_1, t) = E(T_2, t/a_T) \quad (3.74)$$

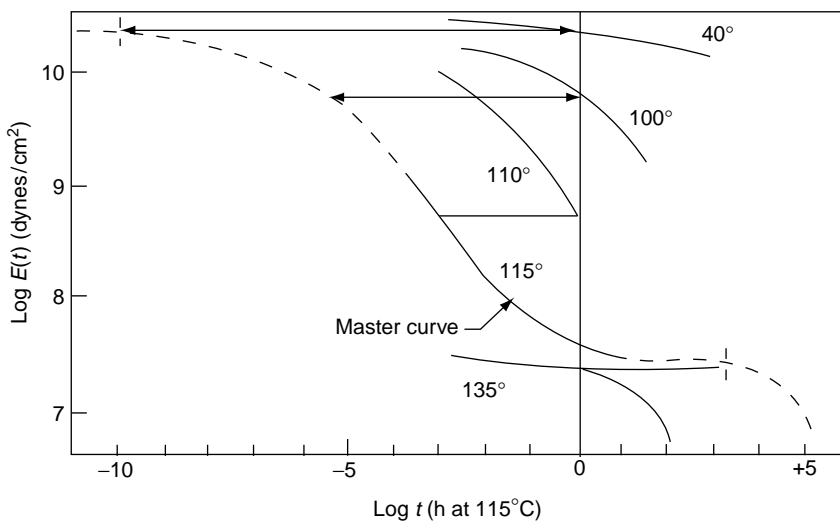


FIGURE 3.20 Modulus-time master curve based on time-temperature superposition of data in Figure 3.19. Times referred to temperature of 115°C.

for a tensile stress relaxation experiment ($T_2 > T_1$). The procedure asserts that the effect of changing the test temperature on viscoelastic properties is the same as that of multiplying or dividing the time scale by a constant quantity (a_T) at each temperature. The quantity a_T is called the *shift factor*, and it must be obtained directly from the experimental curve by measuring the amount of shift along the $\log t$ scale necessary to match the curve. The parameter a_T is chosen as unity at the reference temperature and is a function of the temperature alone, decreasing with increasing temperature.

It is common practice now to use the glass transition temperature (T_g) as the reference temperature for master curve construction. For most amorphous polymers, the shift factor at any other temperature T is then given fairly well by

$$\log_{10} a_T = \log \frac{t(T)}{t(T_g)} = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (3.75)$$

Equation 3.75 is known as the WLF equation (see Equation 3.27) after the initials of the researchers who proposed it [9]. The expression given holds between T_g and $T_g + 100^\circ\text{C}$. However, if a different reference temperature is chosen an equation with the same form as Equation 3.75 can be used, but the constants on the right hand side must be re-evaluated.

The significance of the WLF generalization (Equation 3.75) cannot be over-emphasized. Again and again, one finds in the literature methods of superposing time and temperature for mechanical and other properties in amorphous and partially amorphous materials. Whatever modifications are introduced usually reduce the behavior back in the direction of Equation 3.75.

3.2.15 Dynamic Mechanical Properties

A complete description of the viscoelastic properties of a material requires information over very long times. To supplement creep and stress relaxation measurements which are limited by experimental limitations, experiments are therefore performed in which an oscillating stress or strain is applied to the specimen. These constitute an important class of experiments for studying the viscoelastic behavior of polymeric solids. In addition to elastic modulus, it is possible to measure by these methods the viscous behavior of the material in terms of characteristic damping parameters.

Damping is an engineering material property and the observed response is much more sensitive to the polymer constitution than in step-function experiments. Oscillatory experiments (also referred to as dynamic mechanical experiments) thus offer a powerful technique to study molecular structure and morphology. A significant feature is the breadth of the time-scale spectrum available with these methods, e.g., 10^{-5} – 10^8 cycles/sec.

In a dynamic experiment, the stress will be directly proportional to the strain if the magnitude of the strain is small enough. Then, if the stress is applied sinusoidally the resulting strain will also vary sinusoidally. (The same holds true if the strain is the input and the stress the output.) At sufficiently low frequencies, the strain will follow the stress in phase. However, in the general case the strain will be out of phase.

In the last instance, the strain can be factored into two components—one of which is in phase with the stress and the other which lags behind the stress by $\pi/2$ rad. Alternatively, the stress can be decomposed into a component in phase with the strain and one which leads the strain by $\pi/2$ rad. This is accomplished by use of a rotating vector scheme, as shown in Figure 3.21.

The magnitude of the stress at any time is represented by the projection OC of the vector **OA** on the vertical axis. Vector **OA** rotates with a frequency ω equal to that of the sinusoidally varying stress. The length of **OA** is the stress amplitude (maximum stress) involved in the experiment. The strain is represented by the projection OD of vector **OB** on the vertical axis. The strain vector **OB** rotates in the same direction as **OA** with frequency ω but it lags **OA** by an angle δ . The loss tangent (discussed later) is defined as $\tan \delta$.

The strain vector **OB** can be resolved into vector **OE** along the direction of **OA** and **OF** perpendicular to **OA**. Then the projection OH of **OE** on the vertical axis is the magnitude of the strain which is in phase

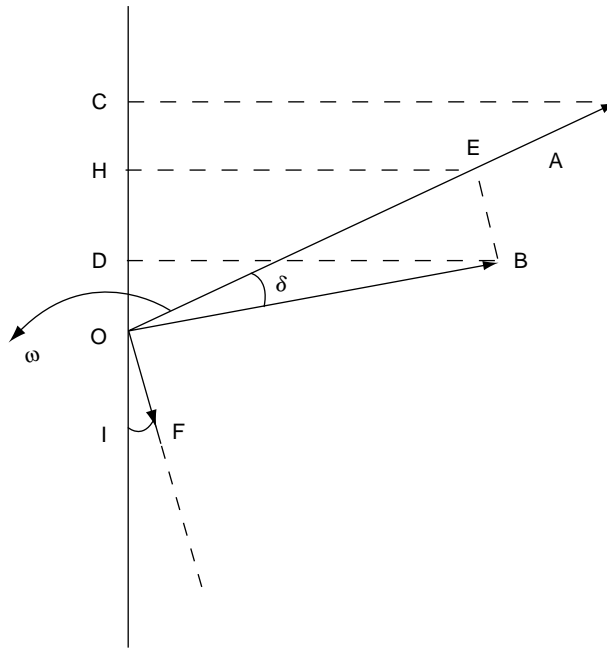


FIGURE 3.21 Decomposition of strain vector into two components in a dynamic experiment.

with the stress at any time. Similarly, projection OI of vector OF is the magnitude of the strain which is $\pi/2$ rad (one quarter cycle) out of phase with the stress.

The stress can be similarly resolved into two components with one along the direction of OB and one leading the strain vector by $\pi/2$ rad. The ratio of the in-phase stress to the strain amplitude (maximum strain) is called the storage modulus. In a shear deformation experiment this quantity is labeled $G'(\omega)$. The ratio of the out-of-phase stress to the strain is the loss modulus $G''(\omega)$.

If, on the other hand, the strain vector is resolved into its components, the ratio of the in-phase strain to stress amplitude (maximum stress) is the storage compliance $J'(\omega)$ and the ratio of the out-of-phase strain to the stress amplitude is the loss compliance $J''(\omega)$.

It is evident from the above description that $G'(\omega)$ and $J'(\omega)$ are associated with the periodic storage and complete release of energy in the sinusoidal deformation process. The loss parameters $G''(\omega)$ and $J''(\omega)$, on the other hand, reflect the nonrecoverable use of applied mechanical energy to cause viscous flow in the material. At a specified frequency and temperature, the dynamic response of a polymer in shear deformation can be summarized by any one of the following pairs of parameters: $G'(\omega)$ and $G''(\omega)$, $J'(\omega)$ and $J''(\omega)$, or absolute modulus $|G|$ and $\tan \delta$.

3.2.15.1 Maxwell Element

As an example, we shall consider the behavior of a Maxwell element in harmonic oscillation. If a sinusoidal force acts on a Maxwell element, the resulting strain will be sinusoidal at the same frequency, but out of phase. The same holds true if the strain is the input and the stress the output. For example, let the strain be a sinusoidal function of time t with a frequency ω rad/sec:

$$\varepsilon = \varepsilon_0 \sin \omega t \quad (3.76)$$

where ε_0 is the maximum or peak strain.

The motion of the Maxwell element (with modulus E and relaxation time $\lambda = \eta/E$) is given by (see Equation 3.36)

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\lambda E} \quad (3.77)$$

The resulting sinusoidal stress (see Appendix A8) is given by

$$\sigma = \varepsilon_0 E \frac{\omega \lambda}{(1 + \omega^2 \lambda^2)^{1/2}} \sin(\omega t + \delta) \quad (3.78)$$

where

$$\delta = \cot^{-1} \omega \lambda \quad (3.79)$$

Thus while the stress will be directly proportional to E , the magnitude will be affected by the products $\omega \lambda$ and will lead the strain by an angle δ . This situation is shown in Figure 3.22.

Instead of working with Equation 3.76 and Equation 3.78, it is easier to work with complex functions. Thus the strain may be written as a complex oscillating function of time with maximum amplitude ε_0 and frequency ω :

$$\varepsilon^* = \varepsilon_0 \exp(i\omega t) \quad (3.80)$$

The real strain is the real part of the complex strain ε^* .

The resulting complex stress σ^* is given (see Appendix A8) by

$$\sigma^* = \varepsilon^* \left[\frac{E\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} + \frac{i(E\omega \lambda)}{1 + \omega^2 \lambda^2} \right] \quad (3.81)$$

The complex elastic (Young's) modulus E^* is expressed as

$$E^* = E' + iE'' = \frac{\sigma^*}{\varepsilon^*} \quad (3.82)$$

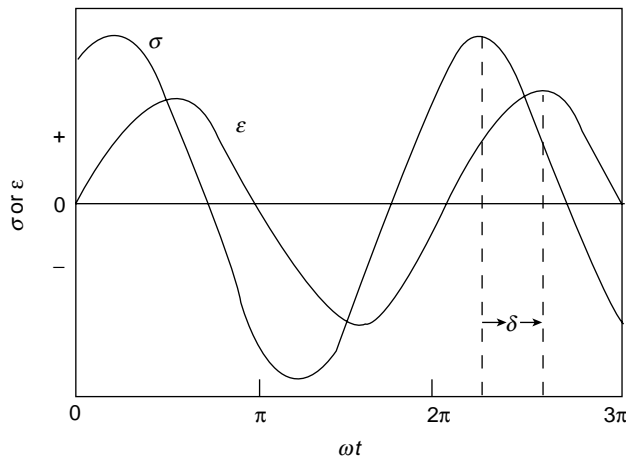


FIGURE 3.22 Strain (ε) and stress (σ) as a function of time (t) on application of a sinusoidal strain to a viscoelastic specimen at a frequency ω .

Identifying Equation 3.81 and Equation 3.82 together, we conclude that

$$E' = \frac{E\omega^2\lambda^2}{1 + \omega^2\lambda^2} \text{ and } E'' = \frac{E\omega\lambda}{1 + \omega^2\lambda^2} \quad (3.83)$$

By the conventions of complex notation we find a loss angle δ , where

$$E^* = [(E')^2 + (E'')^2]^{1/2} \exp(i\delta) \quad \text{and} \quad \tan \delta = \frac{E''}{E'} \quad (3.84)$$

From Equation 3.83 and Equation 3.84,

$$\tan \delta = 1/\omega\lambda \quad (3.85)$$

$$[(E')^2 + (E'')^2]^{1/2} = \frac{E\omega\lambda}{(1 + \omega^2\lambda^2)^{1/2}} \quad (3.86)$$

Another term sometimes used is the dynamic tensile viscosity, $\eta' = E''/\omega$. Using Equation 3.80, Equation 3.84, and Equation 3.86, one further obtains

$$\begin{aligned} \sigma^* = E^* \varepsilon^* &= \frac{E\omega\lambda\varepsilon^*}{(1 + \omega^2\lambda^2)^{1/2}} \exp(i\delta) \\ &= \frac{E\omega\lambda\varepsilon_0}{(1 + \omega^2\lambda^2)^{1/2}} \exp(i\omega t + i\delta) \end{aligned} \quad (3.87)$$

The actual stress σ is the real part of σ^* . Equation 3.87 shows that σ^* depends on E (Hookean model constant) and ε^* but leads by an angle δ . The maximum value of stress σ_0 occurs at $\omega t + \delta = 0$, that is,

$$\sigma_0 = \frac{E\omega\lambda\varepsilon_0}{(1 + \omega^2\lambda^2)^{1/2}} \quad (3.88)$$

$$\sigma^* = \sigma_0 \exp(i\omega t + i\delta) \quad (3.89)$$

By substituting Equation 3.88 in Equation 3.83 we can also write

$$E' = \frac{\sigma_0\omega\lambda}{\varepsilon_0(1 + \omega^2\lambda^2)^{1/2}} \quad (3.90)$$

Thus we can evaluate E , λ , E' , and E'' from experimental measurement of ε_0 , σ_0 , and δ at a known value of ω . In experiments involving shear stress (τ) and shear strain (γ), one evaluates G , λ , G' , and G'' from experimental measurements of γ_0 , τ_0 , and δ at a known value of ω .

The dynamic modulus E' (or G'), which is the real component of E^* (or G^*), is associated with energy storage and release in the periodic deformation and is therefore called the storage modulus. The imaginary part of the modulus, E'' (or G''), is associated with viscous energy dissipation and is a measure of the energy lost per cycle per unit volume (u_e), since

$$u_e = \pi E'' \varepsilon_0^2 \quad (3.91)$$

where, ε_0 is the maximum amplitude of strain. Hence E'' and G'' are called the *loss moduli*. These are the damping terms that give a measure of the dissipation of energy into heat as the material is deformed. The useful damping term called the dissipation factor or loss tangent ($\tan \delta$) is given by (G''/G') or (E''/E') (see Equation 3.84). The value of $\tan \delta$ thus gives a measure of the relative importance of the viscous and elastic behavior of the material.

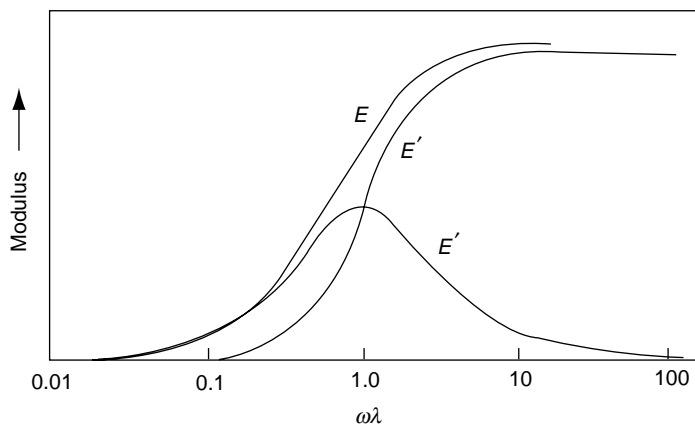


FIGURE 3.23 Dynamic behavior of a Maxwell unit as a function of frequency ω .

The dynamic modulus and damping of a Maxwell unit as a function of frequency are schematically shown in Figure 3.23. The nature of the curves in Figure 3.23 can be explained qualitatively as follows.

At low frequencies, the dynamic modulus is very low as most of the deformation or motion comes from the dashpot (viscous component). At very high frequencies, enough time is not available to allow appreciable flow in the dashpot in a given cycle, and hence the deformation or motion is mostly due to the stretching of the spring such that the dynamic modulus nearly equals the modulus of the spring (elastic component).

At intermediate frequencies, the deformations or motions of both the spring and dashpot take place measurably and in this frequency range, the dynamic modulus (E') increases rapidly with frequency and so also the loss modulus (E''). The latter, however, approaches zero at low as well as high frequencies, and passes through a maximum when the frequency $\omega = 1/\lambda$, where λ is the relaxation time. The absolute value of the modulus E is equal to E'' at low and to E' at high frequencies.

The above discussion also applies to dynamic experiments in shear for which the corresponding moduli are represented by G , G' and G'' .

The analysis presented above for the Maxwell element to explain the significance of dynamic testing can be extended to the Voigt element and corresponding expressions for moduli can be derived. However, models comprised of single elements are useful only as pedagogical tools. They can be combined in series or parallel to yield useful models.

3.2.15.2 Terminology of Dynamic Mechanical Experiments

Dynamic testing is the most commonly used one in the study of polymer properties. Because of its widespread usage, dynamic data have been analyzed in terms of six different functions, as opposed to a single one in stress relaxation and creep. The experiment involves (1) imposition (on a specimen of the material) of either a shear stress or a shear strain which varies sinusoidally with time, and (2) study of the corresponding response.

Using complex functions, the oscillating imposed shear stress and the corresponding shear strain may be written as

$$\tau^*(t) = \tau_0 \exp(i\omega t) \quad (3.92)$$

$$\gamma^*(t) = \gamma_0(\omega) \exp\{i[\omega t - \delta(\omega)]\} \quad (3.93)$$

where $\tau^*(t)$ and $\gamma^*(t)$ are complex functions and $i = \sqrt{-1}$; ω is the frequency of oscillation and τ_0 is its amplitude; $\gamma_0(\omega)$ is the amplitude of the sinusoidal response and $\delta(\omega)$ is the phase difference between stress and strain; and the parenthesis indicates functional dependence.

The dynamic modulus, $G^*(\omega)$, is defined as the ratio of the complex stress to the complex strain

$$G^*(\omega) \equiv \frac{\tau^*(t)}{\gamma^*(t)} = \frac{\tau_0}{\gamma_0(\omega)} e^{i\delta(\omega)} \equiv G_0(\omega) e^{i\delta(\omega)} \quad (3.94)$$

$G_0(\omega)$ and $\delta(\omega)$ represent the first two material properties that can be obtained from dynamic experiments.

The next two material properties are obtained by writing $G^*(\omega)$ in terms of real and imaginary parts as

$$G^*(\omega) = G'(\omega) + iG''(\omega) \quad (3.95)$$

$G'(\omega)$ is referred to as the storage modulus and $G''(\omega)$ as the loss modulus since, as explained before, they are related, respectively, to the energy stored and energy lost in the material. Relationships between $G'(\omega)$, $G''(\omega)$, $G_0(\omega)$ and $\delta(\omega)$ can be written from the fundamentals of complex variables as follows:

$$\begin{aligned} G'(\omega) &= G_0(\omega) \cos[\delta(\omega)] \\ G''(\omega) &= G_0(\omega) \sin[\delta(\omega)] \\ \tan[\delta(\omega)] &= G''(\omega)/G'(\omega) \\ G_0(\omega) &= [\{G'(\omega)\}^2 + \{G''(\omega)\}^2]^{1/2} \end{aligned} \quad (3.96)$$

Alternatively, $\gamma^*(t)$ and $\tau^*(t)$ may be related in terms of complex dynamic compliance, $J^*(\omega)$, as

$$J^*(\omega) \equiv \frac{\gamma^*(t)}{\tau^*(t)} = \frac{\gamma_0(\omega)}{\tau_0} e^{-i\delta(\omega)} \equiv J_0(\omega) e^{-i\delta(\omega)} \quad (3.97)$$

and the complex dynamic compliance may be written in terms of real and imaginary parts, $J'(\omega)$ and $J''(\omega)$, which are termed storage compliance and loss compliance, respectively, as

$$J^*(\omega) = J'(\omega) - iJ''(\omega) \quad (3.98)$$

Again a series of simple algebraic manipulations leads to the following interrelationships:

$$\begin{aligned} G^*(\omega) &= \frac{1}{J^*(\omega)} \\ J'(\omega) &= \frac{G'(\omega)}{\{G'(\omega)\}^2 + \{G''(\omega)\}^2} = \frac{\cos[\delta(\omega)]}{G_0(\omega)} \\ J''(\omega) &= \frac{G''(\omega)}{\{G'(\omega)\}^2 + \{G''(\omega)\}^2} = \frac{\sin[\delta(\omega)]}{G_0(\omega)} \\ \tan[\delta(\omega)] &= J''(\omega)/J'(\omega) \\ G_o^2(\omega) &= \{G'(\omega)\}^2 + \{G''(\omega)\}^2 = \frac{1}{\{J_o(\omega)\}^2} = \frac{2}{\{J'(\omega)\}^2 + \{J''(\omega)\}^2} \end{aligned} \quad (3.99)$$

In the above discussion, six functions $G_0(\omega)$, $\delta(\omega)$, $G'(\omega)$, $G''(\omega)$, $J'(\omega)$, and $J''(\omega)$ have been defined in terms of an idealized dynamic testing, while earlier we defined shear stress relaxation modulus $G(t)$ (see Equation 3.19) and shear creep compliance $J(t)$ (see Equation 3.21) in terms of an idealized stress relaxation experiment and an idealized creep test, respectively. Mathematical relationships relating any one of these eight functions to any other can be derived. Such relationships for interconversion of viscoelastic function are described by Ferry [5], and interested readers are referred to this treatise for the same.

Two reasons can be given as to why so many functions have been defined, especially since the entire information could be presented in terms of only a single one and all the remaining seven functions are

derived from it. First, no single instrument can give the entire dependence of any function over a large enough period of time or frequency extending over several decades. Indeed experimental data are taken with different instruments yielding different material properties and the results are converted in terms of any one desired viscoelastic function.

The second and more important reason for defining so many different functions is that each of these emphasizes different aspects of molecular motions associated with the macroscopic distortion of the material. Thus, in order to gain sufficient insight into these molecular mechanisms, several or all of these functions should be studied.

It should be noted that the treatment in this section is restricted to the study of small deformations; that is, only when the material is subjected either to low shear strains (below about 1%) or to low shear stresses. Under such conditions, the eight material properties are functions of time or frequency only and are independent of the magnitude of the applied shear stress or strain. The material is then said to be in the linear viscoelastic region.

Though most practical applications of polymers would seem to involve much higher stresses, the importance of the study of linear viscoelasticity stems from the fact that it leads to a very sound understanding of the molecular mechanisms of flow and sufficient insight is gained by its study so as to be of immense advantage in the study of large deformations. The study of large deformations, however, is almost empirical, and the reader is referred to several excellent works [10,11].

Rheovibron (dynamic) viscometer is widely used for measurements of dynamic mechanical properties such as loss modulus, storage modulus, and dissipation factor, each as a function of temperature. In this instrument, the test specimen is clamped between strain gauges and subjected to low order of sinusoidal strain at a specified frequency. The value of $\tan \delta$ is directly read and the storage and loss moduli are calculated using sample dimensions and instrument readings.

In a rheometric dynamic spectrometer such as RDS7700 manufactured by Rheometrics, Inc., the torque and normal force generated in response to an imposed motion are measured by a transducer. A microcomputer determines stresses from these values with measured sample motion to calculate strains and viscoelastic functions such as G' , G'' , and $\tan \delta$ [12].

3.2.15.3 Dynamic Mechanical Behavior at Thermal Transitions

Modulus-temperature relations for amorphous polymers in static test reveal a sharp drop of modulus in the glass-to-rubber transition region (see Figure 1.19). Since the storage modulus $G'(\omega)$ behaves like a modulus measured in a static test, it decreases in the glass transition region. However, the loss modulus $G''(\omega)$ and $\tan \delta$ go through a maximum under the same conditions.

Figure 3.24 shows some typical experimental data. It is seen that T_g is easily identifiable as a peak in the $\tan \delta$ or the loss modulus trace. These maxima do not coincide exactly. The maximum in $\tan \delta$ is at a higher temperature than that in $G''(\omega)$, because $\tan \delta$ is the ratio of $G''(\omega)$ and $G'(\omega)$ (see Equation 3.96) and both these moduli are changing in the transition region. At low frequencies (about 1 Hz) the peak in $\tan \delta$ is about 5°C higher than T_g from static measurements or the maximum in the loss modulus-temperature curve.

The development of a maximum in $\tan \delta$ or the loss modulus at the glass-to-rubber transition can be explained as follows. At temperatures below T_g the polymer behaves elastically, and there occurs little or no flow to convert the applied energy into internal work in the material. To explain more explicitly, let h be the energy dissipated as heat per unit volume of material per unit time because of flow in shear deformation. Then

$$h = \sigma(d\gamma/dt) = \eta(d\gamma/dt)^2 \quad (3.100)$$

Thus the work dissipated is proportional to the viscosity (η) of the material at fixed straining rate $d\gamma/dt$.

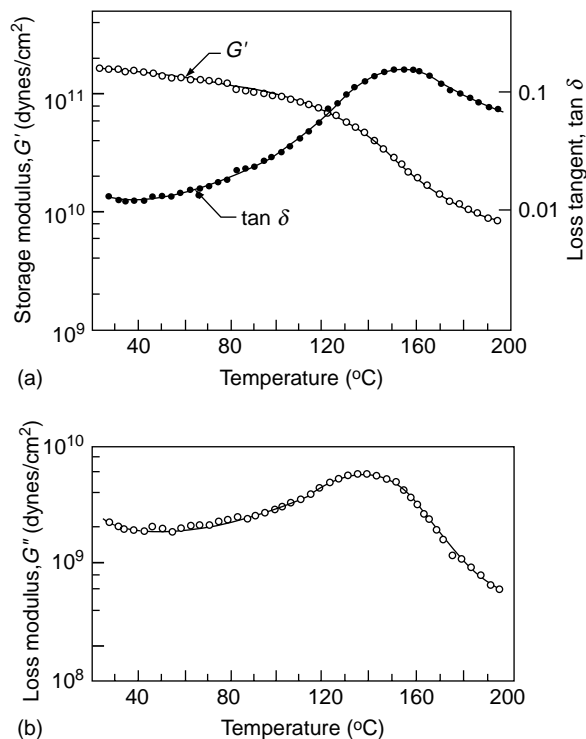


FIGURE 3.24 (a) Storage modulus (G') and loss tangent ($\tan \delta$) for an oriented poly(ethylene terephthalate) fiber; 11 Hz frequency. (b) Loss modulus (G'') for the same fiber.

At low temperatures, η is very high but γ and $d\gamma/dt$ are vanishingly small and h is negligible. As the structure is loosened in the transition region, η decreases but $d\gamma/dt$ becomes much more significant so that h (and hence the loss modulus and $\tan \delta$) increases.

The effective straining rate of polymer segments continues to increase somewhat with temperature above T_g , but η decreases at the same times. The net result is a decrease in damping and a fall-off of the magnitudes of the storage modulus and $\tan \delta$.

3.2.16 Rheological Behavior

Rheology is the science of deformation and flow of matter. Essentially, all thermoplastic resins (and many thermosetting resins) are required to undergo flow in the molten state during the course of product manufacture. Important fabrication processes such as injection, extrusion, and calendering all involve the flow of molten polymers. In plastics fabrication, it is important to understand the effect, on melt viscosity, of such factors as temperature, pressure, rate of shear, molecular weight, and structure. It is also equally important to have reliable means of measuring viscous properties of materials.

The flow behavior of polymeric melts cannot be considered to be purely viscous in character. The response of such materials is more complex, involving characteristics that are both viscous and elastic. This is only to be expected when one is trying to deform variously entangled long-chain molecules with a distribution of molecular weights.

During flow, polymer molecules not only slide past each other, but also tend to uncoil—or at least they are deformed from their equilibrium, random coiled-up configuration. On release of the deforming stresses, these molecules tend to revert to random coiled-up forms. Since molecular entanglements cause the molecules to act in a cooperative manner, some recovery of shape corresponding to the recoiling

occurs. In phenomenological terms, we say that the melt shows elasticity in addition to viscous flow. The elastic—that is to say, time-dependent—effects play a most important part in die swell, extrusion defects, and melt fracture, which will be considered later in this section.

3.2.16.1 Classification of Fluid Behavior

Although one can measure deformation in a solid, one cannot normally do this in a liquid since it undergoes a continuously increasing amount of deformation when a shear stress is applied. But one can determine the deformation rate (the shear rate) caused by an applied shear stress or vice versa, and fluid behavior can be classified on this basis.

We begin by making a reference to Figure 3.25, which schematically illustrates two parallel plates of very large area A separated by a distance r with the space in between filled with a liquid. The lower plate is fixed and a shear force F_s is applied to the top plate of area A producing a shear stress ($\tau = F_s/A$) that causes the plate to move at a uniform velocity v in a direction parallel to the direction of the force.

It may be assumed that the liquid wets the plates and that the molecular layer of liquid adjacent to the stationary plate is stationary while the layer adjacent to the top plate moves at the same velocity as the plate. Intermediate layers of liquid move at intermediate velocities, and at steady state in laminar flow a velocity distribution is established as indicated by the arrows in the diagram. The velocity gradient between the two plates is dv/dr . It is defined as the *shear rate* and is commonly given the symbol $\dot{\gamma}$ i.e.,

$$\dot{\gamma} = dv/dr \quad (3.101)$$

If the liquid is ideal and it is maintained at a constant temperature, the shear stress is linearly and directly proportional to the shear rate such that one may write

$$\tau = \eta(dv/dr) = \eta\dot{\gamma} \quad \text{or} \quad (3.102)$$

$$\eta = \tau/\dot{\gamma} \quad (3.103)$$

where η is the coefficient of viscosity or simply the viscosity or internal friction of the liquid. The linear relationship between τ and $\dot{\gamma}$ given by Equation 3.102 or Equation 3.103 is known as Newton's law and liquids which behave in this manner are called Newtonian fluids or ideal fluids. Other fluids which deviate from Newton's law are described as non-Newtonian. For such fluids, the viscosity defined by Equation 3.103 is also known as the apparent viscosity.

In practice, the Newtonian behavior is confined to low molecular weight liquids. Polymer melts obey Newton's law only at shear rates close to zero and polymer solutions only at concentrations close to zero. The most general rheological equation is

$$\eta = f(\dot{\gamma}, T, t, P, c, \dots) \quad (3.104)$$

where the variables are $\dot{\gamma}$ = shear rate (itself a function of the shear stress), T = temperature, t = time, P = pressure (itself a function of volume), c = concentration, and the multiple dots which follow include, for example, molecular parameters (such as molecular weight and molecular weight distribution), compositional variables (crystallinity and the presence of additives), and factors that relate to processing history. Such an equation is clearly unrealistic, so we shall consider here some of the principal variables, one at a time, assuming that the others remain constant.

Several common types of rheological behavior are shown in Figure 3.26 based upon τ vs. $\dot{\gamma}$ curves. These flow phenotypes are named Newtonian,

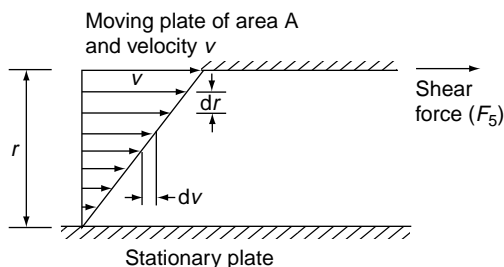


FIGURE 3.25 Velocity distribution of a liquid between two parallel plates, one stationary and the other moving.

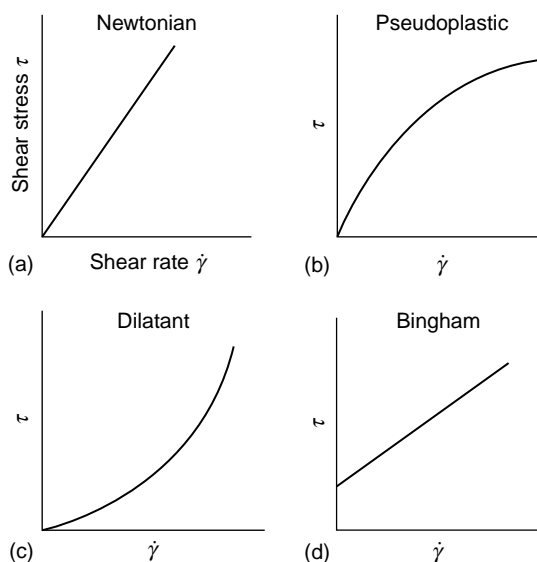


FIGURE 3.26 Flow curves (τ versus $\dot{\gamma}$) for different types of fluid material.

pseudoplastic, dilatant, and Bingham. In Newtonian liquids, the viscosity is constant and independent of shear rate.

In pseudoplastic and dilatant liquids the viscosity is no longer constant. In the former it decreases and in the latter it increases with increasing shear rate; that is to say, the shear stress increases with increasing shear rate less than proportionately in a pseudoplastic and more than proportionately in a dilatant. Pseudoplastics are thus described as shear-thinning and dilatants as shear-thickening fluid systems. These two flow phenotypes can be described by an Equation the ‘power law’:

$$\tau = \eta_N \dot{\gamma}^n \quad (3.105)$$

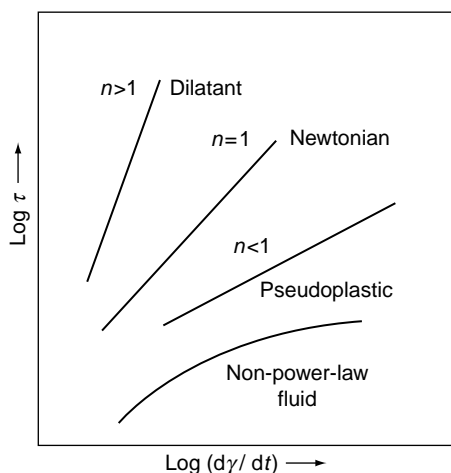


FIGURE 3.27 Power-law plot showing $\log \tau$ versus $\log(d\gamma/dt)$ for different types of fluid material (schematic).

where η_N is the zero shear (Newtonian) viscosity. The exponent n is greater than unity for a dilatant and less than unity for a pseudoplastic. A Newtonian is then seen to be a special case, with $n=1$.

Equation 3.105 gives a linear relationship between $\log \tau$ and $\log \dot{\gamma}$ and the slope of the experimental plot (Figure 3.27) gives the value of n . For the analysis of flow behavior of many systems, the power law relationship has been useful as from a plot of data (Figure 3.27), and measuring the slope, one can readily get an idea of just how non-Newtonian the fluid is.

A Bingham body would be described by the equation

$$\tau - \tau_y = \eta \dot{\gamma} \quad (3.106)$$

where τ_y is the yield stress or yield value. Below τ_y the material will not flow at all (hence $\dot{\gamma} = 0$ and $\eta = \infty$) so that the material, to all intents and

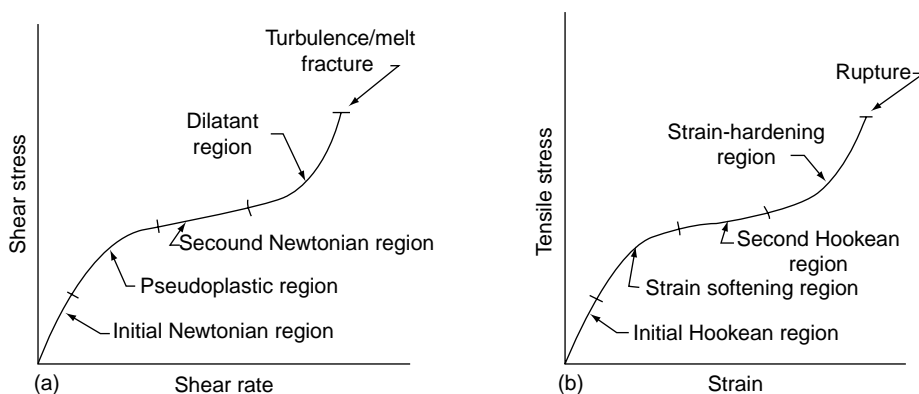


FIGURE 3.28 (a) Generalized flow curve. (b) Typical fully developed stress-strain curve as found in tough plastics under appropriate conditions. The conventional stress has been converted to the true stress.

purposes, is a solid. However, as soon as τ exceeds τ_y , the material suddenly behaves like a liquid with a viscosity that remains constant with increasing shear rate. Materials which exhibit this type of behavior include drilling muds, sewage sludge, toothpaste, greases and fats, as well as the clay slurries originally observed by Bingham.

Lenk [13] has shown that the flow phenotypes form part of a general response pattern which may be summarized in a general flow curve. The generalized flow curve is shown in Figure 3.28 alongside a fully developed stress-strain curve for a typical tough solid in tension after conversion of the conventional stress (i.e., force per unit of original cross-sectional area) to true stress (i.e., force per unit of actual cross-sectional area after deformation). This conversion can be effected if a continuous record of the changes in cross-sectional area of the specimen under test is kept. It may be seen that the shapes of the two curves are absolutely identical and the regions into which the two curves divide have also analogous physical significance.

It is well known that at extremely low shear rates the slope of the $\tau/\dot{\gamma}$ curve (Figure 3.26) is constant and that there exists some very low but finite threshold shear rate beyond which deviation from linearity commences. The slope of the initial linear portion of the curve is known as the 'limiting viscosity,' the zero shear viscosity, or the Newtonian viscosity. Beyond this low shear rate region (initial Newtonian regime) the material is shear-softened (i.e., becomes pseudoplastic), a phenomenon which has its counterpart in the solid state where it is known as strain-softening.

Continuing in the pseudoplastic region it is often found that an upper threshold can be reached beyond which no further reduction in viscosity occurs. The curve then enters a second linear region of proportionality the slope of which is the second Newtonian viscosity.

Polymer melts are almost invariably of the pseudoplastic type, and the existence of first and second Newtonian regions has long been recognized. The pseudoplastic behavior appears to arise from the elastic nature of the melt and from the fact that under shear, polymers tend to be oriented.

At low shear rates Brownian motion of the segments occurs so polymers can coil up (re-entangle) at a faster rate than they are oriented. At higher shear rates such re-entangling rates are slower than the orientation rates and the polymer is hence apparently less viscous. However at very high shear rates (beyond the range of usual interest in the polymer processing industries) the degree of orientation reaches a maximum and so a further decrease in effective viscosity cannot occur; the polymer in this range again becomes Newtonian.

Generally speaking, the larger the polymer molecule the longer the recoiling (re-entangling, relaxation) time so that high-molecular-weight materials tend to be more non-Newtonian at lower shear rates than lower-molecular-weight polymers.

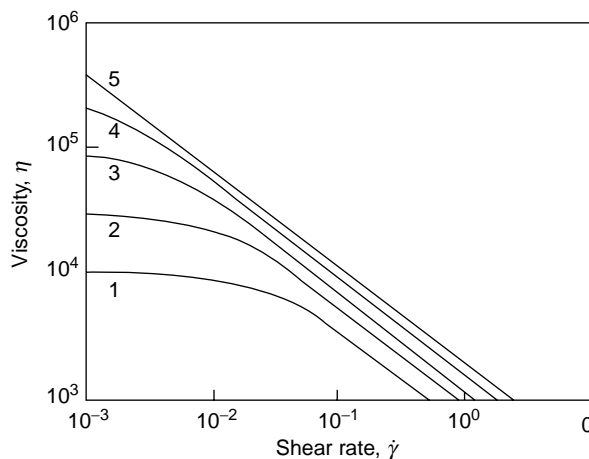


FIGURE 3.29 Typical log viscosity-log shear rate curves at five different temperatures. Curve 1 is for the highest temperature and curve 5 is for the lowest temperature. For a typical polymer, the temperature difference between each curve is approximately 10°C.

The dilatant type is less common among plastics under ordinary conditions, but it can be found in heavily filled systems and in some PVC pastes. The dilatant type (Figure 3.26c) represents the entire generalized flow curve in which the initial Newtonian and pseudoplastic regions have degenerated to a vanishingly small portion of the curve as a whole. In some cases of dilatancy a linear region may be distinguished before the curvature appears. In other cases no distinctly linear portion can be seen at the low-shear-rate end. The Bingham type is not common among plastics.

3.2.16.2 Effect of Shear Rate on Viscosity

Most polymer melts exhibit non-Newtonian behavior with the apparent viscosity decreasing with increasing shear rate (*shear thinning*). Viscosity of polymer at high shear rates may be several orders of magnitude smaller than the viscosity at low shear rates. Typical shear rate vs. viscosity curves are shown in Figure 3.29. The polymer melt has a Newtonian viscosity which is high at very low shear rates. Viscosity decreases nearly linearly with shear rate when plotted on a log-log scale (Figure 3.29). In this linear range, the power law equation (Equation 3.105) with $n < 1$ is applicable.

The reduction of viscosity with increasing rate of shear [14,15] is taken advantage of in achieving desirable and optimum viscosity for polymers in processing machines and equipment without raising the temperature to detrimental levels, simply by raising the shear rate to as high a level as economically and otherwise possible. A reduction in viscosity with increasing shear rate is also taken advantage of in brushing and spraying of paints which are polymer solutions/suspensions containing pigments.

3.2.16.3 Effect of Molecular Weight on Viscosity

The molecular weight of a polymer is the most important factor affecting rheology. For most polymers the zero-shear viscosity is approximately proportional to the weight-average molecular weight (M_w) below a critical value (M_c) and depends on M_w to a power equal to 3.5 at molecular weights above M_c :

$$\eta = K_1 M_w \quad \text{for } M_w < M_c \quad (3.107)$$

and

$$\eta = K_2 M_w^{3.5} \quad \text{for } M_w > M_c \quad (3.108)$$

The relationship between viscosity and molecular weight shown by a graphical logarithmic plot in Figure 3.30 is characterized by a sharp change at the critical molecular weight (M_c). The value of M_c varies from one polymer to another. For most polymers M_c is between 5,000 and 15,000.

The critical molecular weight corresponding to the transition in the viscosity behavior at M_c points to additional hindrance to flow from this point onwards due to chain entanglements. Below this point the molecules usually move independently as in low-molecular-weight liquids, but above this point mutual entanglements of chain molecules is so prominent that movement of one involves dragging of others along with it; as a consequence, increasing molecular weight is associated with a very high rate of viscosity increase.

Considering the fact that the viscosity is increasing logarithmically with molecular weight in Figure 3.30, it should be clear why molecular weight control is important in polymer processing. One needs a molecular weight high enough to attain good mechanical properties but not so high that the molten polymer is too viscous to be processed economically.

The distribution of molecular weights in a polymer also influences its rheology. In general, the broader the range, the lower the shear rate at which shear thinning (decrease in viscosity) develops. Thus polymers with broad molecular-weight distribution are easier to extrude than those with narrow distribution.

Chain branching is another factor that influences flow. The more highly branched a given polymer, the lower will be its hydrodynamic volume and the lower its degree of entanglement at a given molecular weight. One can make the general observation, therefore, that viscosity is higher with linear than with branched polymers at a given shear rate and molecular weight. This does not mean that chain branching is necessarily desirable. In fact, branching results in weaker secondary bonding forces and possibly poorer mechanical properties.

3.2.16.4 Effect of Temperature on Polymer Viscosity

The viscosity of most polymers changes with temperature. An Arrhenius equation of the form

$$\eta = Ae^{E/RT} \quad (3.109)$$

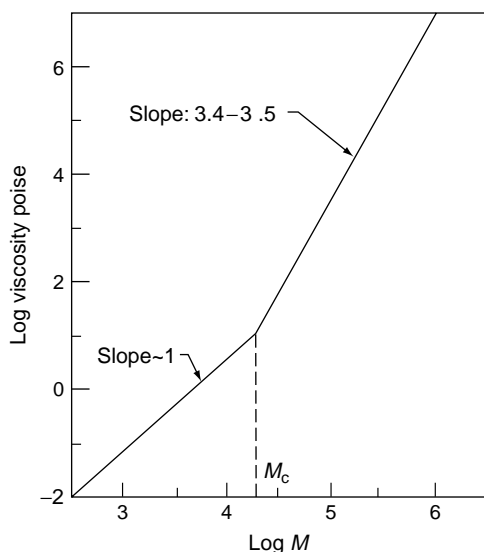


FIGURE 3.30 Dependence of polymer (melt) viscosity on molecular weight (M): a typical plot of log viscosity against log M .

where A is a constant and E is the activation energy, has often been used to relate viscosity and temperature. Constants in the Arrhenius equation can be evaluated by plotting the logarithm of viscosity against the reciprocal of absolute temperature, using shear stress or shear rate as a parameter. The data for most materials give straight line over reasonably large range of temperature.

Whilst the Arrhenius equation can be made to fit experimental data quite well it does nothing to explain the difference between polymers. In this regard, the WLF equation (see Equation 3.27):

$$\log \left(\frac{\eta_T}{\eta_{T_g}} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)}$$

is more useful. Melt viscosity, according to this equation, is a function of $(T - T_g)$. Thus, for example, a major cause of the difference between the viscosity of poly(methacrylate) at its processing temperature (where $T - T_g = 100^\circ\text{C}$) and the

viscosity of polyethylene at its processing temperature (where $T - T_g = 200^\circ\text{C}$) is explicable by this relationship. The WLF equation also explains why viscosity is more temperature sensitive with materials processed closer to their T_g , for example, poly(methyl methacrylate), compared with nylon 6.

3.2.16.5 Effect of Pressure on Viscosity

While temperature rises at constant pressure cause a decrease in viscosity, pressure rises at constant temperature cause an increase in viscosity since this causes a decrease in free volume. It is commonly found that

$$\left(\frac{\partial \eta}{\partial T}\right)_v = 0 \quad (3.110)$$

In other words, if the volume and hence free volume are made constant by increasing pressure as temperature is increased then the viscosity also remains constant. It is in fact found that within the normal processing temperature range for a polymer it is possible to consider an increase in pressure as equivalent, in its effect on viscosity, to a decrease in temperature.

For most polymers an increase in pressure of 100 atm is equivalent to a drop of temperature in the range $30\text{--}50^\circ\text{C}$. It is also found that those polymers most sensitive to temperature changes in their normal processing range are the most sensitive to pressure.

3.2.16.6 Weissenberg Effects

An elastic aftereffect is generally found in high-molecular-weight fluid materials after extrusion under high shear stress through an orifice or die, and this is seen to happen within a fraction of a second after extrusion. Herzog and Weissenberg [16] observed the existence of a “normal” force in polymers subjected to shear stress. In the polymeric melt systems, the entangled polymer chains get deformed elastically during flow and a different kind of force is generated within the flowing melt in addition to the force applied. The additional force generated is manifested as tensile force perpendicular to the shear plane.

This is visualized when a cone with vertical channels and with its axis normal to a plate is rotated with a viscous liquid placed between cone and plate. Liquid will climb into these channels (Figure 3.31a). The arrows in Figure 3.31a indicate that a force exists which acts on the liquid, normal to the shear plane. This force can be measured, without drilling channels into the cone, by placing pressure transducers in contact with the liquid at the cone face and by measuring the pressure exerted on the cone by the liquid.

The effect, known as the Weissenberg effect, is more easily demonstrated by subjecting a viscous liquid mass to shear in a coaxial cylinder system by rotating one while keeping the other fixed (Figure 3.31b). It

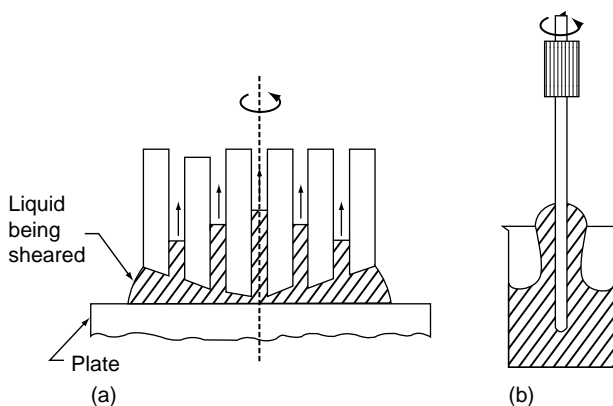


FIGURE 3.31 Experiments demonstrating the normal force (Weissenberg) effect. Liquid climb on rotation (a) in channels drilled into a cone and (b) in a coaxial cylinder.

is most easily demonstrated by rotating the inner cylinder. On rotation, the liquid climbs up the rotating inner rod or cylinder to a significant height.

The Weissenberg effect is clearly manifested in the increase in diameter of extruded profiles of a variety of molten polymers. The extrusion swelling (Figure 3.32), more commonly known as die swell, arises probably due to a combination of normal stress effects and a possible elastic recovery consequent to prior compression before the melt or liquid enters the die.

A practical aspect of the Weissenberg effect or die swell is that, on extrusion or calendaring, the melt coming out is larger than the die or nip size. The control of size is done by partly using a smaller aperture and by partly having an increased draw down. The extrusion, the swelling may be largely minimized by having a conical die design with the narrow end towards the interior and by lowering of melt temperatures, extrusion rates, or molecular weight of the polymer.

3.2.16.7 Irregular Flow or Melt Fracture

Above a certain shear stress considered as the critical shear stress, flow instabilities of many polymer melts exhibited by an abrupt change in the shape of the molten extrudate are found to occur. The irregularities in flow may be due to Reynolds turbulence or structural turbulence and thermo-mechanical breakdown of the polymer [17].

Above the critical shear stress, the material near the wall relaxes very much faster than the core material leading to the flow irregularities, which, according to Tordella [18], is caused by a fracture of the melt before its entry into the die. Polymers that show flow irregularities at low output rates are those that have comparatively long relaxation times. The origin of flow irregularities and the site of melt fracture is near the entrance to the die since this is the zone of greatest shear stress. The stress enhancement is so great compared to the relaxation time that the polymer melt fractures much like a solid.

Melt fracture depends on die geometry, molecular weight, molecular-weight distribution, and chain branching. A linear polymer such as high-density polyethylene is characterized by a higher critical shear stress than the corresponding branched polymer (low-density) polyethylene) of comparable molecular weight.

3.2.17 Measurement of Viscosity

Perhaps the most important factor to a process engineer in predicting extrusion or molding behavior is melt viscosity. Several methods are used to obtain the viscosity of polymer solutions and melts experimentally as a function of shear rate [19]. Instruments for making such measurements must necessarily accomplish two things: (1) the fluid must be sheared at measurable rates, and (2) the stress developed must be known. Two kinds of instruments having simple geometry and wide use are a rotational viscometer and capillary or extrusion rheometer.

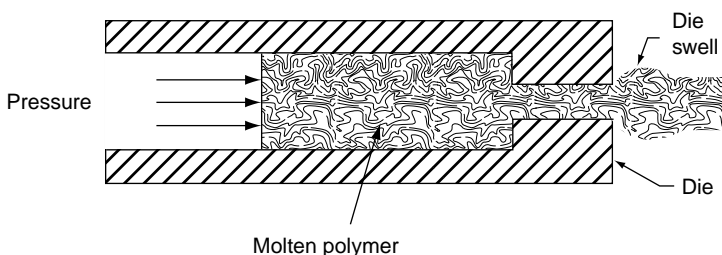


FIGURE 3.32 Schematic representation of polymer flow through a die orifice.

3.2.17.1 Rotational Viscometers

In a rotational viscometer (using cylinders, cones, spheres, and discs) the fluid is sheared at a given temperature in the fluid is sheared at a given temperature in the annular or enclosed space due to rotation of the inner cylinder or the like device while the outer cylinder or device is kept stationary or vice versa. In either case the torque required for the rotation is a measure of the shearing stress and the speed of rotation gives a measure of the rate of shear. Rotational viscometers using coaxial cylinders (Figure 3.33a) measure relatively low viscosity liquids. Typical is the Haake-Rotovisco. In this device, the cup is stationary and the bob is driven through a torsion spring. In a cone-and-plate rotational viscometer (Figure 3.33b), the molten polymer is contained between the bottom plate and the cone, which is rotated at a constant velocity (Ω). Shear stress (τ) is defined as

$$\tau = \frac{3\Phi}{2\pi R_c^3} \quad (3.111)$$

where Φ is the torque in dynes per centimeter (CGS) or in Newtons per meter (SI), and R_c is the cone radius in centimeters or meters. Shear rate ($\dot{\gamma}$) is given by

$$\dot{\gamma} = \frac{\Omega}{\alpha} \quad (3.112)$$

where Ω is the angular velocity in degrees per second (CGS) or in radians per second (SI) and α is the cone angle in degrees or radians. Viscosity is then

$$\eta = \tau/\dot{\gamma} = \frac{3\alpha\Phi}{2\pi R_c^3\Omega} = \frac{k\Phi}{\Omega} \quad (3.113)$$

where ($K = 3\alpha/2\pi R_c^3$) is a constant defined by viscometer design.

An analogous result is obtained if the plate rotates and the cone and plate viscometer is the Weissenberg Rheogoniometer. It consists of a plate that can be rotated at different speeds by means of a constant speed motor-cum-gear assembly (Figure 3.34). The speed of rotation is measured accurately by means of a transducer.

A cone is placed concentrically above the plate, the cone angle being around 1–5°. The cone is supported vertically by a frictionless air bearing and is attached to a firm support through a calibrated torsional spring. Any torque experienced by the cone leads to an equilibrium deflection of this spring

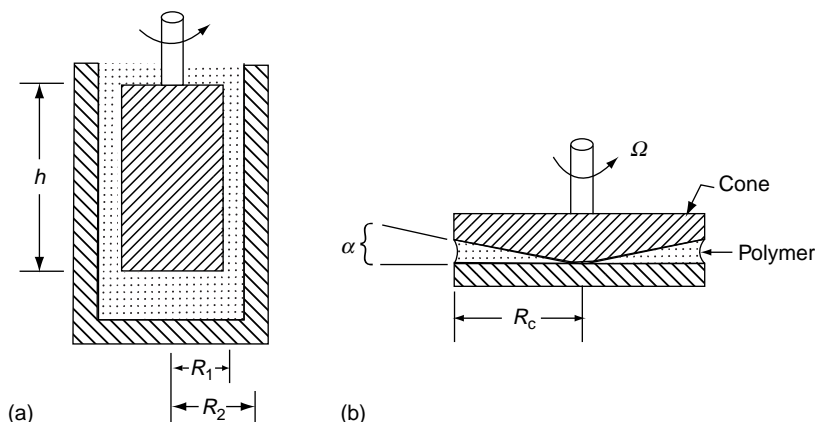


FIGURE 3.33 (a) Coaxial cylinder viscometer. (b) Cone and plate rheometer.

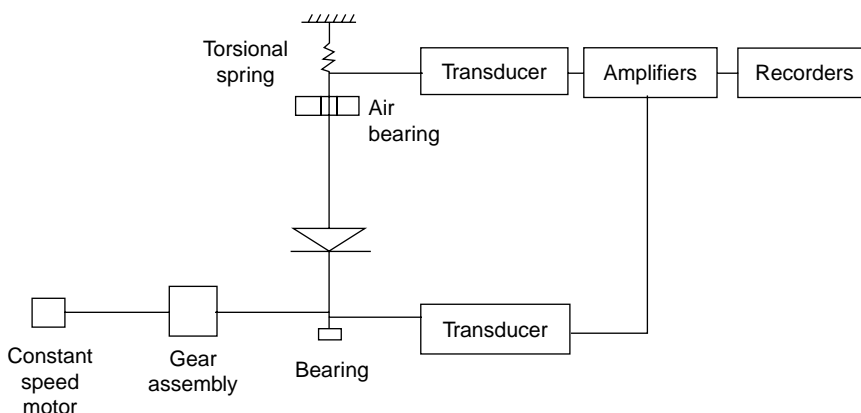


FIGURE 3.34 Scheme of a Weissenberg Rheogoniometer.

which is measured by means of a transducer. The polymer sample is placed in the space between the cone and plate and the torque experienced by the stationary cone is measured for different rotational speeds of the plate.

Relating the shear stress at the cone surface to the measured torque and the shear rate to the angular velocity of the plate, the expression for the viscosity (η) is obtained as

$$\eta = \frac{3K\theta \sin \alpha}{2\pi R_p^3 \omega} \quad (3.114)$$

where K is the torsional constant and θ is the deflection of the spring; R_p is the radius and ω is the angular velocity of the plate; and α is the angle of the cone. While θ and ω are experimentally determined quantities, K and α are obtained by calibration on other materials.

The cone and plate viscometer gives reliable experimental data over an extensive range of shear rates (10^{-4} – 10^4 sec^{-1}). Not only can it be used to measure viscosities in simple shear, but it can also be used to determine the dynamic properties of viscoelastic materials. The unit is also set up to measure the normal stresses exhibited by viscoelastics, i.e., those perpendicular to the plane of shear.

3.2.17.2 Capillary Rheometers

These rheometers are widely used to study the rheological behavior of molten polymers. As shown in Figure 3.35 the fluid is forced from a reservoir into and through a fine-bore tube, or capillary, by either mechanical or pneumatic means. The fluid is maintained at isothermal conditions by electrical temperature control methods. Either the extrusion pressure or volumetric flow rate can be controlled as the independent variable with the other being the measured dependent variable.

Under steady flow and isothermal conditions for an incompressible fluid (assuming only axial flow and no slip at the wall), the viscous force resisting the motion of a column of fluid in the capillary is equal to the applied force tending to move the column in the direction of flow. Thus,

$$\tau = \frac{R\Delta P}{2L} \quad (3.115)$$

where R and L are the radius and length of the column and ΔP is the pressure drop across the capillary. The shear stress τ is therefore zero at the center of the capillary and increases to a maximum value at the capillary wall. This maximum value is the one generally used for the shear stress in capillary flow.

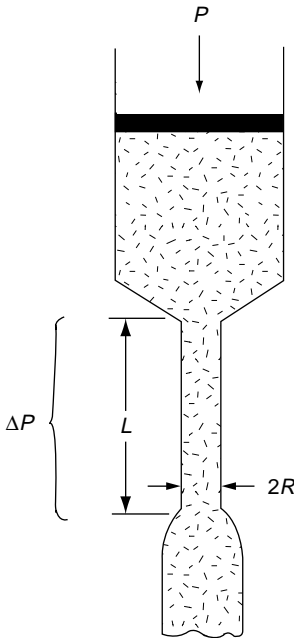


FIGURE 3.35 Capillary rheometer (schematic).

In normal capillary rheometry for polymer melts, the flowing stream exits into the atmosphere, and the driving static pressure in the reservoir is taken to be ΔP . In such cases, end effects involving viscous and elastic deformations at the entrance and exit of the capillary should be taken into account when calculating the true shear stress at the capillary wall, particularly if the ratio of capillary length to radius (L/R) is small.

For a fluid showing Newtonian behavior the shear rate ($\dot{\gamma}$) at the wall is given by

$$\dot{\gamma} = 4Q/\pi R^3 \quad (3.116)$$

where Q is the volumetric flow rate through the capillary under a pressure drop ΔP . Melt viscosity is expressed as

$$\eta = \tau/\dot{\gamma} = \frac{\pi R^4 \Delta P}{8LQ} \quad (3.117)$$

The measured values of polymer flow taken by capillary rheometers are often presented as plots of shear stress versus shear rate at certain temperatures. These values are called apparent shear stress and apparent shear rate at the tube wall. Corrections must be applied to these values in order to obtain true values. The corrected value of shear stress is determined by the Bagley correction [20]

$$\tau_c = \frac{R\Delta P}{2(L + e)} \quad (3.118)$$

where τ_c is the corrected value and e is the length correction expressed as a function of radius.

Correction to the shear rate is necessitated by the fact that unlike in isothermal Newtonian flow where the velocity distribution from wall to wall in a tube is parabolic, nonparabolic velocity profile develops in non-Newtonian flow. The Rabinowitsch correction [21] is applied to shear rate to eliminate this error as follows:

$$\dot{\gamma}_c = \frac{3n + 1}{4n} \dot{\gamma}_a \quad (3.119)$$

where subscript c stands for corrected value and subscript a stands for apparent value of shear rate at tube wall; the correction term n is given by $d \log \tau_a / d \log \dot{\gamma}_a$ and is 1 for Newtonian flow.

There are three main reasons why the capillary rheometer is widely used in the plastics industry: (1) shear rate and flow geometry in capillary rheometer are very similar to conditions actually encountered in extrusion and injection molding; (2) a capillary rheometer typically covers the widest shear rate ranges (10^{-6} sec^{-1} to 10^6 sec^{-1}); and (3) a capillary rheometer provides good practical data and information on the die swell, melt instability, and extrudate defects.

3.2.18 Plastics Fractures

The principal causes of fracture of a plastic part are the prolonged action of a steady stress (creep rupture), the application of a stress in a very short period of time (impact), and the continuous application of a cyclically varying stress (fatigue). In all cases the process of failure will be accelerated if the plastic is in a aggressive environment.

Two basic types of fracture under mechanical stresses are recognized; brittle fracture and ductile fracture. These terms refer to the type of deformation that precedes fracture.

Brittle fractures are potentially more dangerous because there occurs no observable deformation of the material. In a ductile failure, on the other hand, large nonrecoverable deformations occur before rupture actually takes place and serve as a valuable warning. A material thus absorbs more energy when it fractures in a ductile fashion than in a brittle fashion.

In polymeric materials fracture may be ductile or brittle, depending on several variables, the most important of which are the straining rate, the stress system, and the temperature. Both types of failures may thus be observed in the one material, depending on the service conditions.

3.2.19 Impact Behavior of Plastics

Tests of brittleness make use of impact tests. The main causes of brittle failure in materials have been found to be (1) triaxiality of stress, (2) high strain rates, and (3) low temperatures. Test methods developed for determining the impact behavior of materials thus involve striking a notched bar with a pendulum. This is the most convenient way of subjecting the material to triaxiality of stress (at the notch tip) and a high strain rate so as to promote brittle failures.

The standard test methods are the *Charpy* and *Izod* tests, which employ the pendulum principle (Figure 3.36a). The test procedures are illustrated in Figure 3.36b and c. The specimen has a standard notch on the tension side.

In the Charpy test the specimen is supported as a simple beam and is loaded at the midpoint (Figure 3.36b). In the Izod test it is supported as a cantilever and is loaded at its end (Figure 3.36c). The standard energy absorbed in breaking the specimen is recorded.

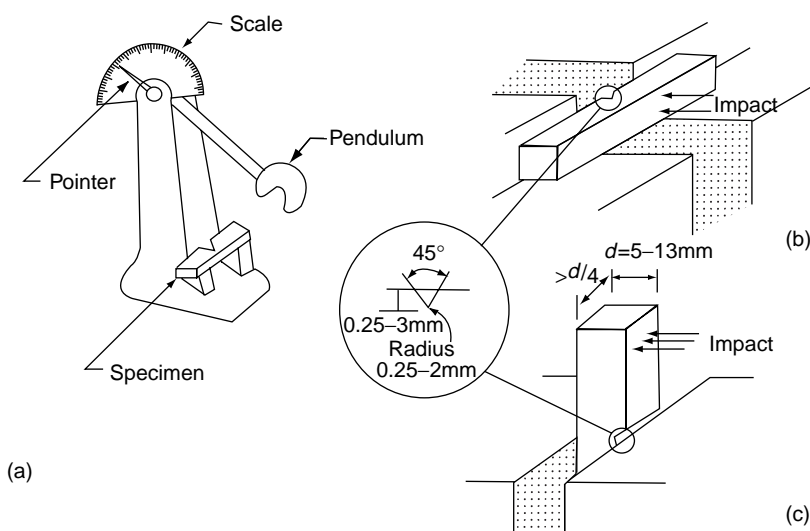


FIGURE 3.36 Impact test. (a) Schematic diagram of Charpy impact testing machine. (b) Arrangement of Charpy impact specimen. (c) Mounting of Izod impact specimen.

The results of impact tests are often scattered, even with the most careful test procedure. A normal practice in such cases is to quote the median strength rather than the average strength, because the median is more representative of the bulk of the results if there is a wide scatter with a few very high or very low results. Impact strengths are normally expressed as

$$\text{Impact} = \frac{\text{Energy absorbed to break}}{\text{Area at notch section}}$$

(ft-lbf/in², cm-kgf/cm², or J/m²)

Occasionally, the less satisfactory term of energy to break per unit width may be quoted in units of ft-lbf/in, cm-kgf/cm or J/m.

The choice of notch depth and tip radius will affect the impact strength observed. A sharp notch is usually taken as a 0.25-mm radius, a blunt notch as a 2-mm radius. The typical variation of impact strength with notch-tip variation for several thermoplastics is presented in Figure 3.37. It is evident that the use of a sharp notch may even rank plastic materials in an order different from that obtained by using a blunt notch. This fact may be explained by considering the total energy absorbed to break the specimen as consisting of energy necessary for crack initiation and for crack propagation.

When the sharp notch (0.25-mm radius) is used, it may be assumed that the energy necessary to initiate the crack is small, and the main contribution to the impact strength is the propagation energy. On this basis Figure 3.37 would suggest that high-density polyethylene and ABS have relatively high crack-propagation energies, whereas materials such as PVC, nylon, polystyrene, and acrylics have low values. The large improvement in impact strength observed for PVC and nylon when a blunt notch is used would imply that their crack-initiation energies are high. On the other hand, the smaller improvement in the impact strength of ABS with a blunt notch would suggest that the crack-initiation energy is low. Thus

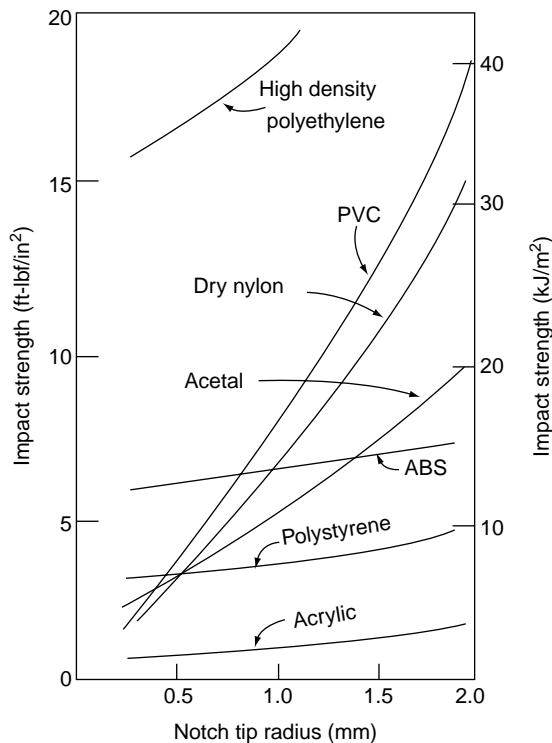


FIGURE 3.37 Variation of impact strength with notch radius for several thermoplastics.

the benefit derived from using rounded corners would be much less for ABS than for materials such as nylon or PVC.

Temperature has a pronounced effect on the impact strength of plastics. In common with metals, many plastic materials exhibit a transition from ductile behavior to brittle as the temperature is reduced. The variation of impact strength with temperature for several common thermoplastics is shown in Figure 3.38.

The ranking of the materials with regard to impact strength is seen to be influenced by the test temperature. Thus, at room temperature (approximately 20°C) polypropylene is superior to acetal; at subzero temperatures (e.g., -20°C) polypropylene does not perform as well as acetal. This comparison pertains to impact behavior measured with a sharp (0.25-mm) notch. Note that notch sharpness can influence the impact strength variation with temperature quite significantly. Figure 3.39 shows that when a blunt (2-mm) notch is used, there is indeed very little difference between acetal and polypropylene at 20°C, whereas at -20°C acetal is much superior to polypropylene.

It may be seen from Figure 3.38 and Figure 3.39 that some plastics undergo a change from ductile or tough (high impact strength) to brittle (low impact strength) behavior over a relatively narrow temperature change. This allows a temperature for ductile-brittle transition to be cited. In other plastic materials this transition is much more gradual, so it is not possible to cite a single value for transition temperature. It is common to quote in such cases a brittleness temperature, $T_B(1/4)$.

This temperature is defined as the value at which the impact strength of the material with a sharp notch (1/4-mm tip radius) is 10 kJ/m² (4.7 ft-lbf/in²). When quoted, it provides an indication of the temperature above which there should be no problem of brittle failure. However, it does not mean that a material should never be used below its $T_B(1/4)$, because this temperature, by definition, refers only to the impact behavior with a sharp notch. When the material is unnotched or has a blunt notch, it may still have satisfactory impact behavior well below $T_B(1/4)$.

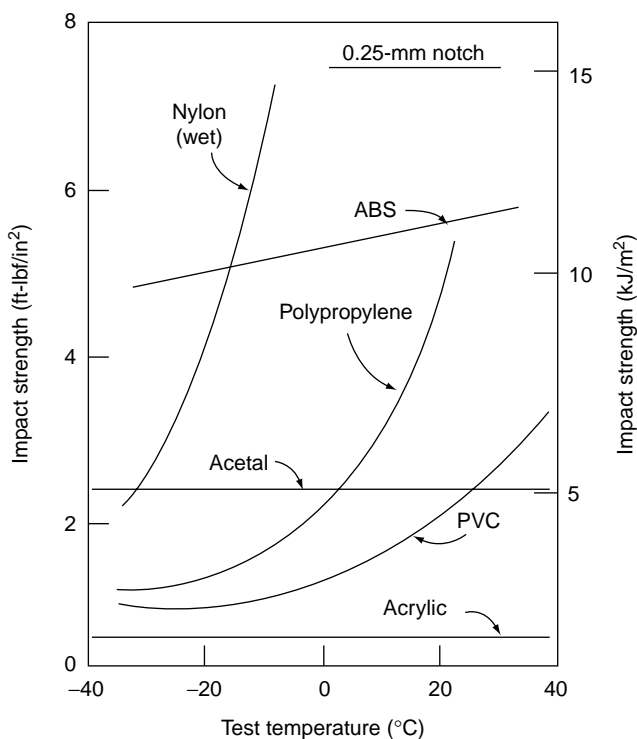


FIGURE 3.38 Variation of impact strength with temperature for several thermoplastics with sharp notch.

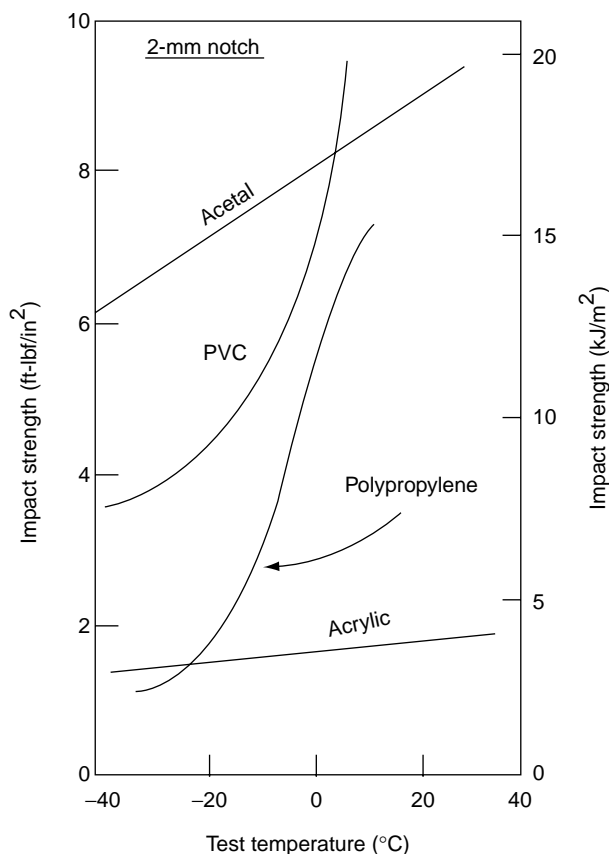


FIGURE 3.39 Variation of impact strength with temperature for several thermoplastics with blunt notch.

Other environmental factors besides temperature may also affect impact behavior. For example, if the material is in the vicinity of a fluid which attacks it, then the crack-initiation energies may be reduced, resulting in lower impact strength. Some materials, particularly nylon, are significantly affected by water, as illustrated in [Figure 3.40](#). The absorption of water produces a spectacular improvement in the impact behavior of nylon.

Note that the method of making the plastic sample and the test specimen can have significant effect on the measured values of the properties of the material. Test specimens may be molded directly or machined from samples which have been compression molded, injection molded, or extruded. Each processing method involves a range of variables, such as melt temperature, mold or die temperature, and shear rate, which influence the properties of the material.

Fabrication defects can affect impact behavior for example, internal voids, inclusion, and additives, such as pigments, which can produce stress concentrations within the material. The surface finish of the specimen may also affect impact behavior. All these account for the large variation usually observed in the results of testing one material processed and/or fabricated in different ways. It also emphasizes the point that if design data are needed for a particular application, then the test specimen must match as closely as possible the component to be designed.

In some applications impact properties of plastics may not be critical, and only a general knowledge of their impact behavior is needed. In these circumstances the information provided in [Table 3.1](#) would be adequate. The table lists the impact behavior of a number of commonly used thermoplastics over a range of temperatures in three broad categories [22].

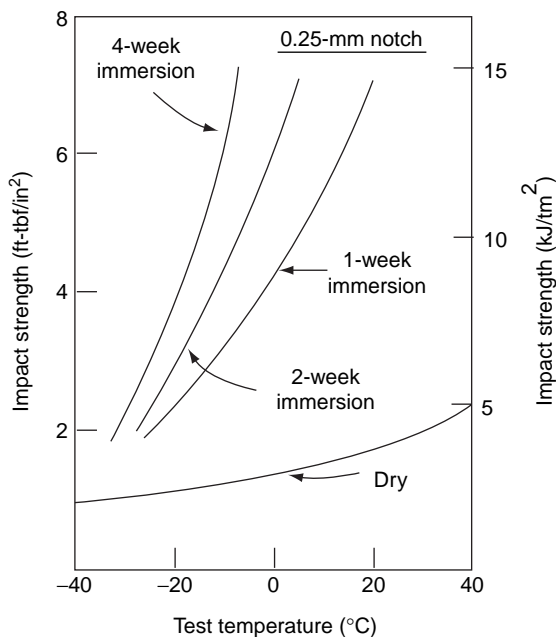


FIGURE 3.40 Effect of water content on impact strength of nylon.

3.2.20 Fatigue of Plastics

A material subject to alternating stresses over long periods may fracture at stresses much below its maximum strength under static loading (tensile strength) due to the phenomenon called fatigue. Fatigue has been recognized as one of the major causes of fracture in metals. Although plastics are susceptible to a wider range of failure mechanisms, it is likely that fatigue still plays an important part in plastics failure.

TABLE 3.1 Impact Behavior of Common Thermoplastics over a Range of Temperatures

Plastic Material	Temperature (°C)							
	−20	−10	0	10	20	30	40	50
Polyethylene (low density)	A	A	A	A	A	A	A	A
Polyethylene (high density)	B	B	B	B	B	B	B	B
Polypropylene	C	C	C	C	B	B	B	B
Polystyrene	C	C	C	C	C	C	C	C
Poly(methyl methacrylate)	C	C	C	C	C	C	C	C
ABS	B	B	B	B	B	B	A	A
Acetal	B	B	B	B	B	B	B	B
Teflon	B	A	A	A	A	A	A	A
PVC (rigid)	B	B	B	B	B	B	A	A
Polycarbonate	B	B	B	B	A	A	A	A
Poly(phenylene oxide)	B	B	B	B	B	B	A	A
Poly(ethylene terephthalate)	B	B	B	B	B	B	B	B
Nylon (dry)	B	B	B	B	B	B	B	B
Nylon (wet)	B	B	B	A	A	A	A	A
Glass-filled nylon (dry)	C	C	C	C	C	C	C	B
Polysulfone	B	B	B	B	B	B	B	B

A, tough (specimens do not break completely even when sharply notched); B, notch brittle; C, brittle even when unnotched.

For metals the fatigue process is generally well understood and is divided into three stages crack initiation, crack growth, and fracture. Fatigue theory of metals is well developed, but the fatigue theory of polymers is not. The completely different molecular structure of polymers means that there is unlikely to be a similar type of crack initiation process as in metals, though it is possible that once a crack is initiated the subsequent phase of propagation and failure may be similar.

Fatigue cracks may develop in plastics in several ways. If the plastic article has been machined, surface flaws capable of propagation may be introduced. However, if the article has been molded, it is more probable that fatigue cracks will develop from within the bulk of the material. In a crystalline polymer the initiation of cracks capable of propagation may occur through slip of molecules. In addition to acting as a path for crack propagation, the boundaries of spherulites (see Chapter 11), being areas of weakness, may thus develop cracks during straining. In amorphous polymers cracks may develop at the voids formed during viscous flow.

A number of features are peculiar to plastics, which make their fatigue behavior a complex subject not simply analyzed. Included are viscoelastic behavior, inherent damping, and low thermal conductivity. Consider, for example, a sample of plastic subjected to a cyclic stress of fixed amplitude. Because of the high damping and low thermal conductivity of the material, some of the input energy will be dissipated in each cycle and appear as heat. The temperature of the material will therefore rise, and eventually a stage will be reached when the heat transfer to the surroundings equals the heat generation in the material. The temperature of the material will stabilize at this point until a conventional metal-type fatigue failure occurs.

If, in the next test, the stress amplitude is increased to a higher value, the material temperature will rise further and stabilize, followed again by a metal-type fatigue failure. In Figure 3.41, where the stress amplitude has been plotted against the logarithm of the number of cycles to failure, failures of this type have been labeled as fatigue failures. This pattern will be repeated at higher stress amplitudes until a point is reached when the temperature rise no longer stabilizes but continues to rise, resulting in a short-term thermal softening failure in the material. At stress amplitudes above this crossover point there will be thermal failures in an even shorter time. Failures of this type have been labeled as thermal failures in Figure 3.41. The fatigue curves in Figure 3.41 thus have two distinct regimes—one for the long-term conventional fatigue failures, and one for the relatively short-term thermal softening failures.

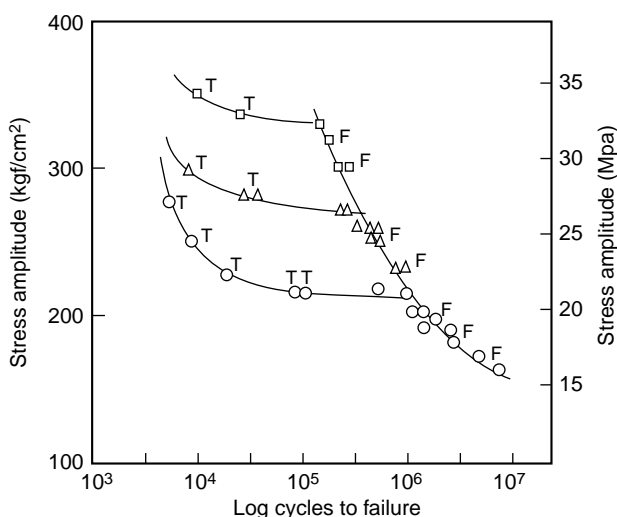


FIGURE 3.41 Typical fatigue behavior of a thermoplastic at several frequencies, F, fatigue failure; T, thermal failure, ○, 5.0 Hz; Δ, 1.67 Hz; □, 0.5 Hz. (Adapted from Crawford, R. J. 1981. *Plastics Engineering*, Pergamon, London.)

The frequency of the cyclic stress would be expected to have a pronounced effect on the fatigue behavior of plastics, a lower frequency promoting the conventional-type fatigue failure rather than thermal softening failure. Thus it is evident from Figure 3.41 that if the frequency of cycling is reduced, then stress amplitudes which would have produced thermal softening failures at a higher frequency may now result in temperature stabilization and eventually fatigue failure. Therefore, if fatigue failures are required at relatively high stresses, the frequency of cycling must be reduced.

Normally, fatigue failures at one frequency on the extrapolated curve fall from the fatigue failures at the previous frequency (Figure 3.41). As the cyclic stress amplitude is further reduced in some plastics, the frequency remaining constant, the fatigue failure curve becomes almost horizontal at large values of the number of stress cycles (N). The stress amplitude at which this leveling off occurs is clearly important for design purposes and is known as the fatigue limit. For plastics in which fatigue failure continues to occur even at relatively low stress amplitudes, it is necessary to define an endurance limit—that is, the stress amplitude which would not cause fatigue failure up to an acceptably large value of N .

3.2.21 Hardness

Hardness of a material may be determined in several ways: (1) resistance to indentation, (2) rebound efficiency, and (3) resistance to scratching. The first method is the most commonly used technique for plastics. Numerous test methods are available for measuring the resistance of a material to indentation, but they differ only in detail. Basically they all use the size of an indent produced by a hardened steel or diamond indenter in the material as an indication of its hardness—the smaller the indent produced, the harder the material, and so the greater the hardness number. Hardness tests are simple, quick, and nondestructive, which account for their wide use for quality control purposes.

3.2.22 Indentation Hardness

The test methods used for plastics are similar to those used for metals. The main difference is that because plastics are viscoelastic allowance must be made for the creep and the time-dependent recovery which occurs as a result of the applied indentation load.

3.2.22.1 Brinell Hardness Number

A hardened steel ball 10 mm in diameter is pressed into the flat surface of the test specimen under load of 500 kg for 30 sec. The load is then removed, and the diameter of the indent produced is measured (Figure 3.42). The Brinell hardness number (BHN) is then defined as

$$\text{BHN} = \frac{\text{Load applied to indenter (kgf)}}{\text{Contact area of indentation (mm}^2\text{)}} = \frac{2P}{\pi D(D - \sqrt{D^2 - d^2})} \quad (3.120)$$

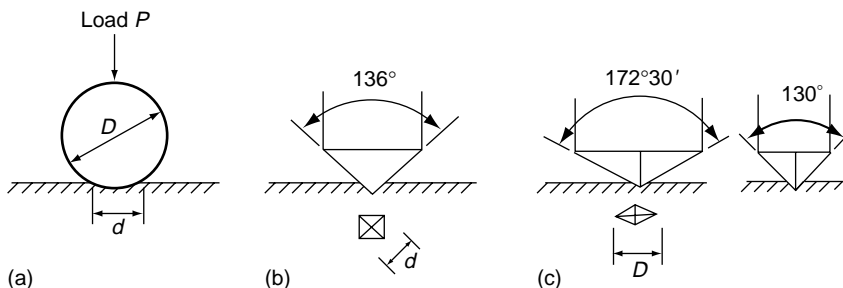


FIGURE 3.42 Indentation hardness tests. (a) Brinell test. (b) Vickers test. (c) Knoop test.

where D is the diameter of the ball and d is the diameter of the indent. Tables are available to convert the diameter of the indent into BHN.

Although the units of Brinell hardness are kgf/mm^2 , it is quoted only as a number. A disadvantage of the Brinell hardness test when used for plastics is that the edge of the indent is usually not well defined. This problem is overcome in the following test.

3.2.22.2 Vickers Hardness Number

The Vickers hardness test differs from the Brinell test in that the indenter is a diamond (square-based) pyramid (Figure 3.42) having an apex angle of 136° . If the average diagonal of the indent is d , the hardness number is calculated from

$$\text{Vickers hardness number} = \frac{\text{Load applied to indenter (kgf)}}{\text{Contact area of indentation (mm}^2\text{)}} = 1.854 \left(\frac{P}{d^2} \right) \quad (3.121)$$

As in the Brinell test, tables are available to convert the average diagonal into Vickers number.

3.2.22.3 Knoop Hardness Number

The indenter used in the Knoop hardness is a diamond pyramid, but the lengths of the two diagonals, as shown in Figure 3.42, are different. If the long diagonal of the indent is measured as D , the hardness number is obtained from

$$\text{Knoop hardness number} = 14.23 \left(\frac{P}{D^2} \right) \quad (3.122)$$

Time-dependent recovery of the indentation in plastics is a problem common to all three tests. To overcome this problem, allow a fixed time before making measurements on the indent.

3.2.22.4 Rockwell Hardness Number

The Rockwell test differs from the other three tests because the depth of the indent rather than its surface area is taken as a measure of hardness. A hardened steel ball is used as the indenter. A major advantage of the Rockwell test is that no visual measurement of the indentation is necessary, and the depth of the indent is read directly as a hardness value on the scale.

The test involves three steps, as shown in Figure 3.43. A minor load of 10 kg is applied on the steel ball, and the scale pointer is set to zero within 10 sec of applying the load. In addition to this minor load, a major load is applied for 15 sec. A further 15 sec after removal of the major load (with the minor load still on the ball), the hardness value is read off the scale. Since creep and recovery effects can influence readings, it is essential to follow a defined time cycle for the test.

Several Rockwell scales (Table 3.2) are used, depending on the hardness of the material under test (Table 3.3). The scale letter is quoted along with the hardness number e.g., Rockwell R60. Scales R and L are used for low-hardness number, e.g., Rockwell R60. Scales R and L are used for low-hardness materials, and scales M and E when the hardness value is high. When the hardness number exceeds 115 on any scale, the sensitivity is lost, so another scale should be used.

3.2.22.5 Barcol Hardness

The Barcol hardness tester is a hand-operated hardness measuring device. Its general construction is shown in Figure 3.44. With the back support leg placed on the surface, the instrument is gripped in the hand and its measuring head is pressed firmly and steadily onto the surface until the instrument rests on the stop ring. The depth of penetration of the spring-loaded indenter is transferred by a lever system to an indicating dial, which is calibrated from 0 to 100 to indicate increasing hardness. To allow for creep, one normally takes readings after 10 sec.

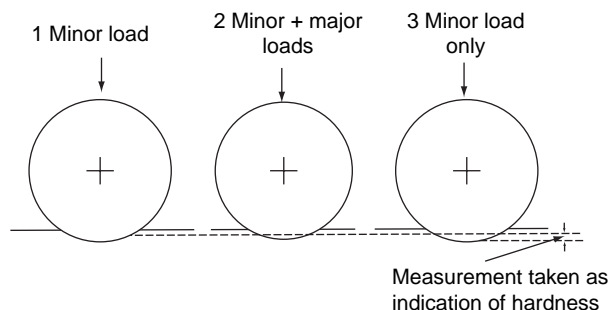


FIGURE 3.43 Stages in Rockwell hardness test: 1, minor load; 2, minor and major loads; 3, minor load only.

The indenter in the Barcol tester Model No. 934-1 is a truncated steel cone having an included angle of 26° with a flat tip of 0.157 mm (0.0062 in.) in diameter. The values obtained using this instrument are found to correlate well to Rockwell values on the M scale. This instrument is used for metals and plastics. Two other models, No. 935 and No. 936, are used for plastics and very soft materials, respectively.

3.2.22.6 Durometer Hardness

A durometer is an instrument for measuring hardness by pressing a needle-like indenter into the specimen. Operationally, a durometer resembles the Barcol tester in that the instrument is pressed onto the sample surface until it reaches a stop ring. This forces the indenter into the material, and a system of levers transforms the depth of penetration into a pointer movement on an indicating dial, which is calibrated from 0–100.

The two most common types of durometers used for plastics are the Shore Type A and Shore Type D. They differ in the spring force and the geometry of the indenter, as shown in [Figure 3.45](#). Due to creep, readings should be taken after a fixed time interval, often chosen as 10 sec. Typical hardness values of some of the common plastics measured by different test methods are shown in [Table 3.4](#).

3.2.23 Rebound Hardness

The energy absorbed when an object strikes a surface is related to the hardness of the surface: the harder the surface, the less the energy absorbed, and the greater the rebound height of the object after impact. Several methods have been developed to measure hardness in this way. The most common method uses a *Shore scleroscope*, in which the hardness is determined from the rebound height after the impact of a diamond cone dropped onto the surface of the test piece. Typical values of Scleroscope hardness together with the Rockwell M values (in parentheses) for some common plastics are as follows: PMMA 99 (M 102), LDPE 45 (M 25), polystyrene 70 (M 83), and PVC 75 (M 60).

TABLE 3.2 Rockwell Hardness Scales

Scale	Major Load (kg)	Dia. of Indenter (in.)
R	60	1/2
L	60	1/4
M	100	1/4
E	100	1/8

TABLE 3.3 Choice of Hardness Test Methods Based on Modulus Range of Plastics

	Material	Test Method
<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> <div style="height: 100px; border-left: 1px solid black; position: relative;"> <div style="position: absolute; top: 0; left: -5px;">↑</div> <div style="position: absolute; bottom: 0; left: -5px;">↓</div> </div> </div> <div> <div>Low modulus</div> <div>High modulus</div> </div> </div>	Rubber	Shore A or BS 903
	Plasticized PVC	Shore A or BS 2782
	Low-density polyethylene	Shore D
	Medium-density polyethylene	Shore D
	High-density polyethylene	Shore D
	Polypropylene	Rockwell R
	Toughened polystyrene	Rockwell R
	ABS	Rockwell R
	Polystyrene	Rockwell M
	Poly(methyl methacrylate)	Rockwell M

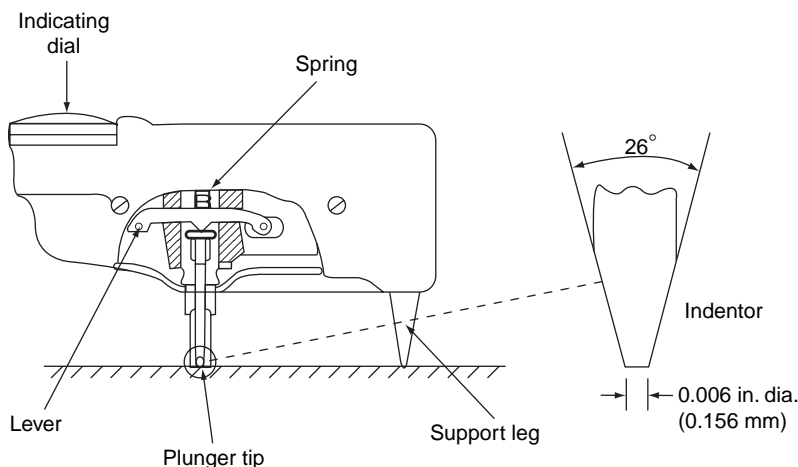
3.2.24 Scratch Hardness

Basically, scratch hardness is a measure of the resistance the test sample has to being scratched by other materials. The most common way of qualifying this property is by means of the Mohs scale. On this scale various materials are classified from 1 to 10. The materials used, as shown in [Figure 3.46](#), range from talc (1) to diamond (10). Each material on the scale can scratch the materials that have a lower Mohs number; however, the Mohs scale is not of much value for classifying plastic materials, because most common plastics fall in the 2–3 Mohs range. However, the basic technique of scratch hardness may be used to establish the relative merits of different plastic materials from their ability to scratch one another.

Scratch hardness is particularly important in plastics used for their optical properties and is usually determined by some of mar-resistance test. In one type of test a specimen is subjected to an abrasive treatment by allowing exposure to a controlled stream of abrasive, and its gloss (specular reflection) is measured before and after the treatment. In some tests the light transmission property of the plastic is measured before and after marring.

3.2.25 Stress Corrosion Cracking of Polymers

Stress corrosion cracking of polymers occurs in a corrosive environment and also under stress [23,24]. This kind of crack starts at the surface and proceeds at right angles to the direction of stress. The amount

**FIGURE 3.44** General construction of Barcol hardness tester.

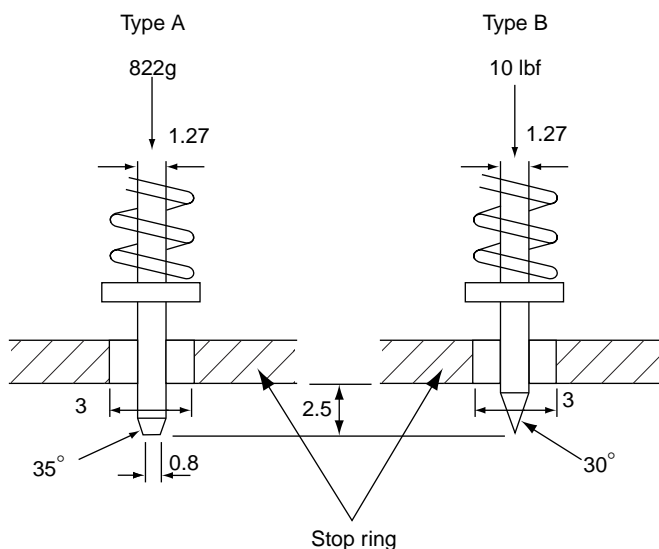


FIGURE 3.45 Two types of Shore durometer.

of stress necessary to cause stress corrosion cracking is much lower than the normal fracture stress, although there is a minimum stress below which no stress corrosion cracking occurs.

The stress corrosion resistance of polymers depends on the magnitude of the stress, the nature of the environment, the temperature, and the molecular weight of the specimen. Ozone cracking is a typical example of stress corrosion cracking of polymers. The critical energy for crack propagation (τ_c) in ozone cracking varies very little from one polymer to another and is about 100 erg/cm² (0.1 J/m²). This value is much lower than the τ_c values for mechanical fracture, which are about 10⁷ erg/cm² (10⁴ J/m²).

In ozone cracking very little energy is dissipated in plastic or viscoelastic deformations at the propagating crack, and that is why τ_c is about the same as the true surface energy. The only energy supplied to the crack is that necessary to provide for the fresh surfaces due to propagation of the crack, because in ozone cracking chemical bonds at the crack tip are broken by chemical reaction, so no high stress is necessary at the tip.

The critical energy τ_c is about 4,000 erg/cm² for PMMA in methylated spirits at room temperature, but the value is lower in benzene and higher in petroleum ether. Thus τ_c in this case is much higher than the true surface energy but still much lower than that for mechanical crack propagation.

TABLE 3.4 Some Typical Hardness Values for Plastics

Material	Brinell	Vickers	Knoop	Rockwell	Barcol	Shore D
High-density Polyethylene	4	2		R40		70
Polypropylene	7	6		R100		74
Polystyrene	25	7	17	M83	76	74
Poly(methyl methacrylate)	20	5	16	M102	80	90
Poly(vinyl chloride)	11	9		M60		80
Poly(vinyl chloride-co-vinyl acetate)	20	5	14	M75		
Polycarbonate		7		M70	70	60
Nylon		5	15	M75		80
Cellulose acetate	12	4	12	M64		70

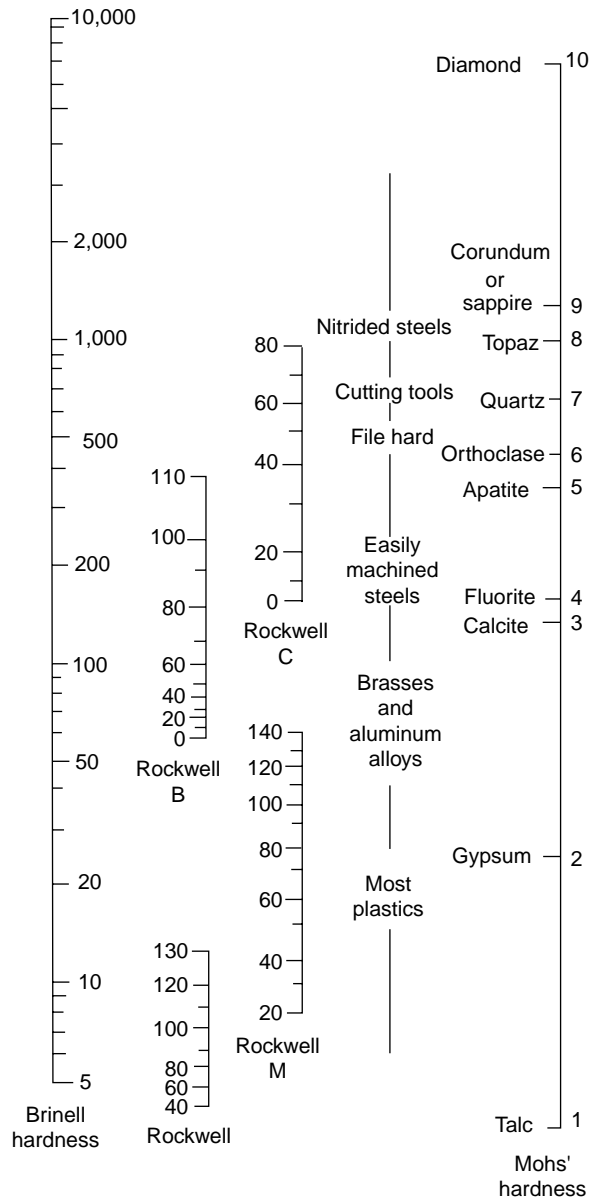


FIGURE 3.46 Comparison of hardness scales (approximate).

3.3 Reinforced Plastics

The modulus and strength of plastics can be increased significantly by means of reinforcement [25–27]. A reinforced plastic consists of two main components—a matrix, which may be either a thermoplastic or thermosetting resin, and a reinforcing filler, which is mostly used in the form of fibers (but particles, for example glass spheres, are also used).

The greater tensile strength and stiffness of fibers as compared with the polymer matrix is utilized in producing such composites. In general, the fibers are the load-carrying members, and the main role of the matrix is to transmit the load to the fibers, to protect their surface, and to raise the energy for crack

TABLE 3.5 Typical Properties of Reinforcing Fibers

Fiber	Density (g/cm ³)	Tensile Strength		Tensile Modulus	
		10 ⁴ kgf/cm ²	GPa	10 ⁵ kgf/cm ²	GPa
E Glass	2.54–2.56	3.5–3.7	3.4–3.6	7.1–7.7	70–76
Carbon	1.75–2.0	2.1–2.8	2.1–2.8	24.5–40.8	240–400
Asbestos	2.5–3.3	2.1–3.6	2.1–3.5	14.3–19.4	140–190
Boron	2.6	3.0–3.6	3.0–3.5	40.8–45.9	400–450
Silicon carbide	3.2–3.4	3.0–3.7	3.0–3.6	46.9–50.0	460–490
Kevlar-49	1.45	3.0–3.6	3.0–3.6	13.2	130

Source: Crawford, R. J. 1981. *Plastic Engineering*, Pergamon, London.

propagation, thus preventing a brittle-type fracture. The strength of the fiber-reinforced plastics is determined by the strength of the fiber and by the nature and strength of the bond between the fibers and the matrix.

3.3.1 Types of Reinforcement

The reinforcing filler usually takes the form of fibers, since it is in this form that the maximum strengthening of the composite is attained. A wide range of amorphous and crystalline materials can be used as reinforcing fibers, including glass, carbon, asbestos, boron, silicon carbide, and more recently, synthetic polymers (e.g., Kevlar fibers from aromatic polyamides). Some typical properties of these reinforcing fibers are given in Table 3.5.

Glass is relatively inexpensive, and in fiber form it is the principal form of reinforcement used in plastics. The earliest successful glass reinforcement had a low-alkali calcium–alumina borosilicate composition (E glass) developed specifically for electrical insulation systems. Although glasses of other compositions were developed subsequently for other applications, no commercial glass better than E glass has been found for plastics reinforcement. However, certain special glasses having extra high-strength properties or modulus have been produced in small quantities for specific applications (e.g., aerospace technology).

Glass fibers are usually treated with finishes. The function of a finish is to secure good wetting and to provide a bond between the inorganic glass and the organic resin. The most important finishes are based on silane compounds—e.g., vinyltrichlorosilane or vinyltriethoxysilane.

3.3.2 Types of Matrix

The matrix in reinforced plastics may be either a thermosetting or thermoplastic resin. The major thermosetting resins used in conjunction with glass-fiber reinforcement are unsaturated polyester resins and, to a lesser extent, epoxy resins. These resins have the advantage that they can be cured (cross-linked) at room temperature, and no volatiles are liberated during curing.

Among thermoplastic resins used as the matrix in reinforced plastics, the largest tonnage group is the polyolefins, followed by nylon, polystyrene, thermoplastic polyesters, acetal, polycarbonate, and polysulfone. The choice of any thermoplastic is dictated by the type of application, the service environment, and the cost.

3.3.3 Analysis of Reinforced Plastics

Fibers exert their effect by restraining the deformation of the matrix while the latter transfers the external loading to the fibers by shear at the interface. The resultant stress distributions in the fiber and the matrix tend to be complex. Theoretical analysis becomes further complicated because fiber length, diameter, and

orientation are all factors. A simplified analysis follows for two types of fiber reinforcement commonly used, namely, (1) continuous fibers and (2) discontinuous fibers.

3.3.3.1 Continuous Fibers

We will examine what happens when a load is applied to an ideal fiber composite in which the matrix material is reinforced by fibers which are uniform, continuous, and arranged uniaxially, as shown in Figure 3.47a.

Let us assume that the fibers are gripped firmly by the matrix so that there is no slippage at the fiber-matrix interface and both phases act as a unit. Under these conditions the strains in the matrix and in the fiber under a load are the same (Figure 3.47b), and the total load is shared by the fiber and the matrix:

$$P_c = P_m + P_f \quad (3.123)$$

where P is the load and the subscripts c, m, and f refer, respectively, to composite, matrix and fiber.

Since the load $P = \sigma A$, Equation 3.123, expressed in terms of stresses (σ) and cross-sectional areas (A), becomes

$$\sigma_c A_c = \sigma_m A_m + \sigma_f A_f \quad (3.124)$$

Rearranging gives

$$\sigma_c = \sigma_m \left(\frac{A_m}{A_c} \right) + \sigma_f \left(\frac{A_f}{A_c} \right) \quad (3.125)$$

Since the fibers run throughout the length of the specimen, the ratio A_m/A_c can be replaced by the volume fraction $\Phi_m = V_m/V_c$, and similarly A_f/A_c by Φ_f . Equation 3.125 thus becomes

$$\sigma_c = \sigma_m \Phi_m + \sigma_f \Phi_f \quad (3.126)$$

Equation 3.126 represents the rule of mixture for stresses. It is valid only for the linear elastic region of the stress-strain curve (see Figure 3.2). Since $\Phi_m + \Phi_f = 1$, we can write

$$\sigma_c = \sigma_m (1 - \Phi_f) + \sigma_f \Phi_f \quad (3.127)$$

Since the strains on the components are equal,

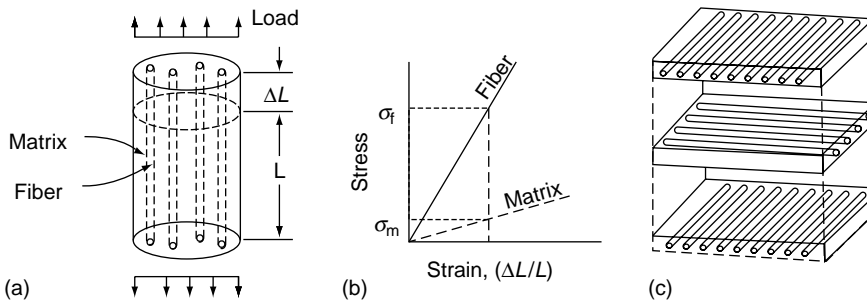


FIGURE 3.47 (a) Continuous-fiber reinforced composite under tensile load. (b) Iso-strain assumption in a composite. (c) Arrangement of fibers in a cross-ply laminate.

$$\varepsilon_c = \varepsilon_m = \varepsilon_f \quad (3.128)$$

Equation 3.126 can now be rewritten to give the rule of mixture for moduli

$$E_c \varepsilon_c = E_m \varepsilon_m \Phi_m + E_f \varepsilon_f \Phi_f$$

i.e.,

$$E_c = E_m \Phi_m + E_f \Phi_f \quad (3.129)$$

Equation 3.128 also affords a comparison of loads carried by the fiber and the matrix. Thus for elastic deformation Equation 3.128 can be rewritten as

$$\frac{\sigma_c}{E_c} = \frac{\sigma_m}{E_m} = \frac{\sigma_f}{E_f}$$

or

$$\frac{P_f}{P_m} = \frac{E_r}{E_m} \left(\frac{A_f}{A_m} \right) = \frac{E_f}{E_m} \left(\frac{\Phi_f}{\Phi_m} \right) \quad (3.130)$$

Because the modulus of fibers is usually much higher than that of the matrix, the load on a composite will therefore be carried mostly by its fiber component (see Example 3.4). However, a critical volume fraction of fibers (Φ_{crit}) is required to realize matrix reinforcement. Thus for Equation 3.127 and Equation 3.130 to be valid, $\Phi_f > \Phi_{\text{crit}}$.

The efficiency of reinforcement is related to the fiber direction in the composite and to the direction of the applied stress. The maximum strength and modulus are realized in a composite along the direction of the fiber. However, if the load is applied at 90° to the filament direction, tensile failure occurs at very low stresses, and this transverse strength is not much different than the matrix strength. To counteract this situation, one uses cross-ply laminates having alternate layers of unidirectional fibers rotated at 90°, as shown in Figure 3.47c. (A more isotropic composite results if 45° plies are also inserted.) The stress-strain behavior for several types of fiber reinforcement is compared in Figure 3.48.

As already noted, if the load is applied perpendicularly to the longitudinal direction of the fibers, the fibers exert a relatively small effect. The strains in the fibers and the matrix are then different, because they act independently, and the total deformation is thus equal to the sum of the deformations of the two phases.

$$V_c \varepsilon_c = V_m \varepsilon_m + V_f \varepsilon_f \quad (3.131)$$

Dividing Equation 3.131 by V_c and applying Hooke's law, since the stress is constant, give

$$\frac{\sigma}{E_c} = \frac{\sigma \Phi_m}{E_m} + \frac{\sigma \Phi_f}{E_f} \quad (3.132)$$

Dividing by σ and rearranging, we get

$$E_c = \frac{E_m E_f}{E_m \Phi_f + E_f \Phi_m} \quad (3.133)$$

The fiber composite thus has a lower modulus in transverse loading than in longitudinal loading.

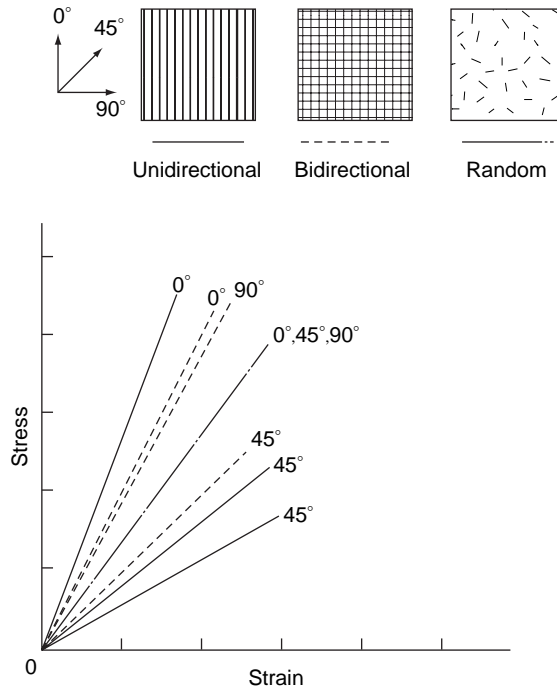


FIGURE 3.48 Stress-strain behavior for several types of fiber reinforcement.

Example 4

A unidirectional fiber composite is made by using 75% by weight of E glass continuous fibers (sp. gr. 2.4) having a Young's modulus of $7 \times 10^5 \text{ kg/cm}^2$ (68.6 GPa), practical fracture strength of $2 \times 10^4 \text{ kg/cm}^2$ (1.9 GPa), and an epoxy resin (sp. gr. 1.2) whose modulus and tensile strength, on curing, are found to be 10^5 kg/cm^2 (9.8 GPa) and $6 \times 10^2 \text{ kg/cm}^2$ (58.8 MPa), respectively. Estimate the modulus of the composite, its tensile strength, and the fractional load carried by the fiber under tensile loading. What will be the value of the modulus of the composite under transverse loading?

Answer. Volume fraction of glass fibers (Φ_f)

$$= \frac{0.75/2.4}{0.75/2.4 + 0.25/1.2} = 0.60$$

$$\Phi_m = 1 - 0.6 = 0.4$$

From Equation 3.129,

$$E_c = 0.4(10^5) + 0.6(7 \times 10^5) = 4.6 \times 10^5 \text{ kg/cm}^2 (45 \text{ GPa})$$

From Equation 3.126,

$$\sigma_c = 0.4(6 \times 10^2) + 0.6(2 \times 10^4) = 1.22 \times 10^4 \text{ kg/cm}^2 (1.2 \text{ GPa})$$

Equation 3.130, on rearranging, gives

$$\frac{P_f}{P_c} = \frac{E_t}{E_c} \Phi_f = \frac{7 \times 10^5}{4.6 \times 10^5} \times 0.6 = 0.91$$

Thus, nearly 90% of the load is carried by the fiber, and the weakness of the plastic matrix is relatively unimportant.

For transverse loading, from Equation 3.133,

$$E_c = \frac{10^5(7 \times 10^5)}{0.6 \times 10^5 + 0.4(7 \times 10^5)} = 2 \times 10^5 \text{ kg/cm}^2 \text{ (19.6 GPa)}$$

Equation 3.127 and Equation 3.129 apply to ideal fiber composites having uni-axial arrangement of fibers. In practice, however, not all the fibers are aligned in the direction of the load. This practice reduces the efficiency of the reinforcement, so Equation 3.127 and Equation 3.129 are modified to the forms

$$\sigma_c = \sigma_m(1 - \phi_f) + k_1 \sigma_f \phi_f \quad (3.134)$$

$$E_c = E_m(1 - \phi_f) + k_2 E_f \phi_f \quad (3.135)$$

If the fibers are bi-directional (see Figure 3.48), then the strength and modulus factors, k_1 and k_2 , are about 0.3 and 0.65, respectively.

3.3.3.2 Discontinuous Fibers

If the fibers are discontinuous, the bond between the fiber and the matrix is broken at the fibers ends, which thus carry less stress than the middle part of the fiber. The stress in a discontinuous fiber therefore varies along its length. A useful approximation pictures the stress as being zero at the end of the filler and as reaching the maximum stress in the fiber at a distance from the end (Figure 3.49a).

The length over which the load is transferred to the fiber is called the transfer length. As the stress on the composite is increased, the maximum fiber stress as well as the transfer length increase, as shown in Figure 3.49a, until a limit is reached, because the transfer regions from the two ends meet at the middle of the fiber (and so no further transfer of stress can take place), or because the fiber fractures. For the latter objective to be reached, so as to attain the maximum strength of the composite, the fiber length must be greater than a minimum value called the critical fiber length, l_c .

Consider a fiber of length l embedded in a polymer matrix, as shown in Figure 3.49b. One can then write, equating the tensile load on the fiber with the shear load on the interface,

$$\frac{\sigma \pi d^2}{4} = \tau \pi d l \quad (3.136)$$

where σ is the applied stress, d is the fiber diameter, and τ is the shear stress at the interface.

The critical fiber length, l_c , can be derived from a similar force balance for an embedded length of $l_c/2$. Thus,

$$l_c = \frac{\sigma_{ff} d}{2\tau_i}$$

and

$$\frac{l_c}{d} = \frac{\sigma_{ff}}{2\tau_i} \quad (3.137)$$

where σ_{ff} is the fiber strength and τ_i is the shear strength of the interface or the matrix, whichever is smaller.

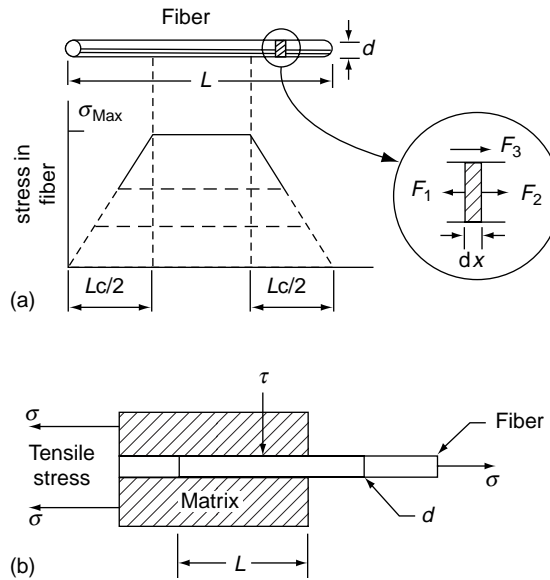


FIGURE 3.49 Composite reinforced with discontinuous fibers. (a) A total length l_c at the two ends of a fiber carries less than the maximum stress. (b) Interfacial strength of the matrix fiber.

So if the composite is to fail through tensile fracture of the fiber rather than shear failure due to matrix flow at the interface between the fiber and the matrix, the ratio l_c/d , known as the critical aspect ratio, must be exceeded, or, in other words, for a given diameter of fiber, d , the critical fiber length, l_c , must be exceeded.

If the fiber length is less than l_c , the matrix will flow around the fiber, and maximum transfer of stress from matrix to fiber will not occur. Using Equation 3.137, we can estimate the value of l_c/d from the values of σ_{ff} and τ_i , and vice versa. Typical values of l_c/d for glass fiber and carbon fiber in an epoxy resin matrix are 30–100 and 70, respectively.

If the fibers are discontinuous, then, since the stress is zero at the end of the fiber, the average stress in the fibers will be less than the value σ_{fmax} , which it would have achieved if the fibers had been continuous over the whole length of the matrix. The value of the average stress will depend on the stress distribution in the end portions of the fibers and also on their lengths. If the stress distributions are assumed to be as shown in Figure 3.49a, then the average stress in the fibers may be obtained as follows.

Considering a differential section of the fiber as shown in Figure 3.49a, we obtain

$$F_1 = \sigma_f \frac{\pi d^2}{4}$$

$$F_2 = \left(\sigma_f + \frac{d\sigma_f}{dx} dx \right) \frac{\pi d^2}{4}$$

$$F_3 = \tau \pi d \, dx$$

For equilibrium,

$$F_1 = F_2 + F_3$$

so,

$$\sigma_f \frac{\pi d^2}{4} = \left(\sigma_f + \frac{d\sigma_f}{dx} dx \right) \frac{\pi d^2}{4} dx + \tau \pi d dx$$

$$\frac{d}{4} d\sigma_f = -\tau dx$$
(3.138)

Integrating gives

$$\frac{d}{4} \int_0^{\sigma_f} d\sigma_f = - \int_{l/2}^x \tau dx$$

$$\sigma_f = \frac{4\tau(l/2 - x)}{d}$$
(3.139)

Three cases may now be considered.

3.3.3.3 Fiber Length Less than l_c

In this case the peak stress occurs at $x=0$ (Figure 3.50a). So from Equation 3.139,

$$\sigma_f = \frac{2\tau l}{d}$$

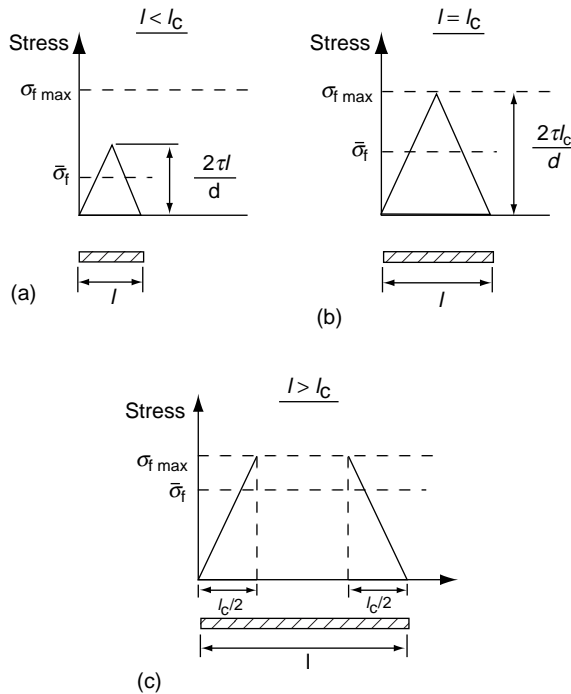


FIGURE 3.50 Stress variation for short and long fibers.

The average fiber stress is obtained by dividing the area of the stress-fiber length diagram by the fiber length; that is,

$$\bar{\sigma}_f = \frac{(l/2)2\tau l/d}{l} = \frac{\tau l}{d}$$

The stress, σ_c , in the composite is now obtained from Equation 3.134

$$\sigma_c = \sigma_m(1 - \Phi_f) + \frac{\tau l k_1}{d} \phi_f \quad (3.140)$$

3.3.3.4 Fiber Length Equal to l_c

In this case the peak value of stress occurs at $x=0$ and is equal to the maximum fiber stress (Figure 3.50b). So

$$\sigma_f = \sigma_{fmax} = \frac{2\tau l_c}{d} \quad (3.141)$$

$$\text{Average fiber stress} = \bar{\sigma}_f = \frac{1}{2} \frac{l_c(2\tau l_c/d)}{l_c}$$

i.e.,

$$\bar{\sigma}_f = \frac{\tau l_c}{d}$$

So from Equation 3.134,

$$\sigma_c = \sigma_m(1 - \phi_f) + k_1 \left(\frac{\tau l_c}{d} \right) \phi_f \quad (3.142)$$

3.3.3.5 Fiber Length Greater than l_c

1. For $l/2 > x > (l - l_c)/2$ (Figure 3.50c),

$$\sigma_f = \frac{4\tau}{d} \left(\frac{1}{2} l - x \right)$$

2. For $(l - l_c)/2 > x > 0$ (Figure 3.50c),

$$\sigma_f = \text{constant} = \sigma_{fmax} = \frac{2\tau l_c}{d}$$

The average fiber stress, from the area under the stress-fiber length graph, is

$$\bar{\sigma}_f = \frac{(l_c/2)\sigma_{fmax} + (l - l_c)\sigma_{fmax}}{l} = \left(1 - \frac{l_c}{2l} \right) \sigma_{fmax} \quad (3.143)$$

So from Equation 3.134,

$$\sigma_c = \sigma_m(1 - \phi_f) + k_1 \phi_f \left(1 - \frac{l_c}{2l}\right) \phi_{fmax}. \quad (3.144)$$

It is evident from Equation 3.143 that to get the average fiber stress as close as possible to the maximum fiber stress, the fibers must be considerably longer than the critical length. At the critical length the average fiber stress is only half of the maximum fiber stress, i.e., the value achieved in continuous fibers (Figure 3.50c).

Equations such as Equation 3.144 give satisfactory agreement with the measured values of strength and modulus for polyester composites reinforced with chopped strands of glass fibers. These strength and modulus values are only about 20%–25% of those achieved by reinforcement with continuous fibers.

Example 5

Calculate the maximum and average fiber stresses for glass fibers of diameter 15 μm and length 2 mm embedded in a polymer matrix. The matrix exerts a shear stress of 40 kgf/cm^2 (3.9 MPa) at the interface, and the critical aspect ratio of the fiber is 50.

Answer.

$$\text{Since } l > l_c, \text{ then} \quad l_c = 50 \times 15 \times 10^{-3} = 0.75 \text{ mm}$$

$$\sigma_{max} = \frac{2\tau l_c}{d} = 2 \times 40 \times 50 = 4 \times 10^3 \text{ kgf/cm}^2 (= 392 \text{ MPa})$$

Also,

$$\bar{\sigma}_f = \left(1 - \frac{l_c}{2l}\right) \sigma_{fmax} = \left(1 - \frac{0.75}{2 \times 2}\right) (4 \times 10^3) = 3.25 \times 10^3 \text{ kgf/cm}^2 (= 318 \text{ MPa})$$

3.3.4 Deformation Behavior of Fiber-Reinforced Plastic

As we have seen, the presence of fibers in the matrix has the effect of stiffening and strengthening it. The tensile deformation behavior of fiber-reinforced composites depends largely on the direction of the applied stress in relation to the orientation of the fibers, as illustrated in Figure 3.48. The maximum strength and modulus are achieved with unidirectional fiber reinforcement when the stress is aligned with the fibers (0°), but there is no enhancement of matrix properties when the stress is applied perpendicular to the fibers. With random orientation of fibers the properties of the composite are approximately the same in all directions, but the strength and modulus are somewhat less than for the continuous-fiber reinforcement.

In many applications the stiffness of a material is just as important as its strength. In tension the stiffness per unit length is given the product EA , where E is the modulus and A is the cross-sectional area. When the material is subjected to flexure, the stiffness per unit length is a function of the product El , where I is the second moment of area of cross section (see Example 3.2). Therefore the stiffness in both tension and flexure increases as the modulus of the material increases, and the advantages of fiber reinforcement thus become immediately apparent, considering the very high modulus values for fibers.

3.3.5 Fracture of Fiber-Reinforced Plastics

Although the presence of the reinforcing fibers enhances the strength and modulus properties of the base material, they also cause a complex distribution of stress in the materials. For example, even under simple tensile loading, a triaxial stress system is set up since the presence of the fiber restricts the lateral contraction of the matrix. This system increases the possibility of brittle failure in the material. The type of fracture which occurs depends on the loading conditions and fiber matrix bonding.

3.3.5.1 Tension

With continuous-fiber reinforcement it is necessary to break the fibers before overall fracture can occur. The two different of fracture which can occur in tension are shown in Figure 3.51. It is interesting to note that when an individual fiber in a continuous-fiber composite breaks, it does not cease to contribute to the strength of the material, because the broken fiber then behaves like a long short fiber and will still be supporting part of the external load at sections remote from the broken end. In short-fiber composites, however, fiber breakage is not an essential prerequisite to complete composite fracture, especially when the interfacial bond is weak, because the fibers may then be simply pulled out of the matrix as the crack propagates through the latter.

3.3.5.2 Compression

In compression the strength of glass-fiber reinforced plastics is usually less than in tension. Under compressive loading, shear stresses are set up in the matrix parallel to the fibers. The fiber aligned in the loading direction thus promote shear deformation. Short-fiber reinforcement may therefore have advantages over continuous fibers in compressive loading because in the former not all the fibers can be aligned, so the fibers which are inclined to the loading plane will resist shear deformation. If the matrix-fiber bond is weak, debonding may occur, causing longitudinal cracks in the composite and buckling failure of the continuous fibers.

3.3.5.3 Flexure or Shear

In flexure or shear, as in the previous case of compression, plastics reinforced with short fibers are probably better than those with continuous fibers, because in the former with random orientation of fibers at least some of the fibers will be correctly aligned to resist the shear deformation. However, with continuous-fiber reinforcement if the shear stresses are on planes perpendicular to the continuous fibers, then the fibers will offer resistance to shear deformation. Since high volume fraction (ϕ_f) can be achieved with continuous fibers, this resistance can be substantial.

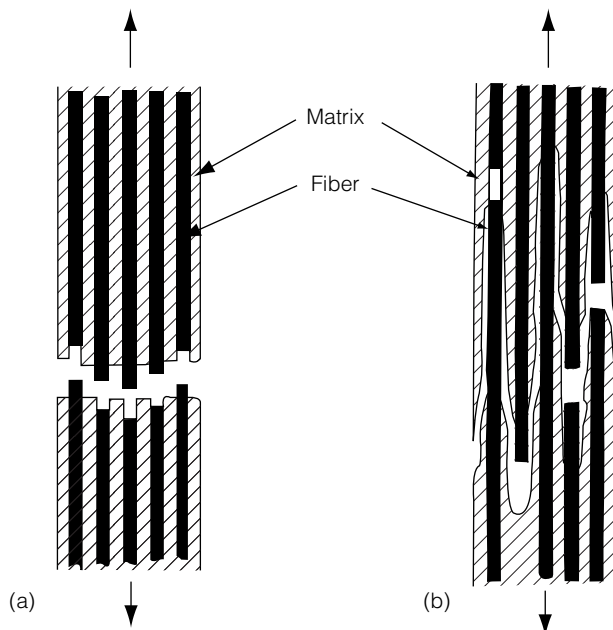


FIGURE 3.51 Typical fracture modes in fiber-reinforced plastics. (a) Fracture due to strong interfacial bond. (b) Jagged fracture due to weak interfacial bond.

3.3.6 Fatigue Behavior of Reinforced Plastics

Like unreinforced plastics, reinforced plastics are also susceptible to fatigue. There is, however, no general rule concerning whether glass reinforcement enhances the fatigue endurance of the base material. In some cases the unreinforced plastic exhibits greater fatigue endurance than the reinforced material; in other cases, the converse is true.

In short-fiber glass-reinforced plastics, cracks may develop relatively easily at the interface close to the ends of the fibers. The cracks may then propagate through the matrix and destroy its integrity long before fracture of the composite takes place. In many glass-reinforced plastics subjected to cyclic tensile stresses, debonding many occur after a few cycles even at modes stress levels. Debonding may be followed by resin cracks at higher stresses, leading eventually to the separation of the component due to intensive localized damage. In other modes of loading, e.g., flexure or torsion, the fatigue endurance of glass-reinforced plastics is even worse than in tension. In most cases the fatigue endurance is reduced by the presence of moisture.

Plastics reinforced with carbon and boron, which have higher tensile moduli than glass, are stiffer than glass-reinforced plastics and are found to be less vulnerable to fatigue.

3.3.7 Impact Behavior of Reinforced Plastics

Although it might be expected that a combination of brittle reinforcing fibers and a brittle matrix (e.g., epoxy or polyester resins) would have low impact strength, this is not the case, and the impact strengths of the fibers or the matrix. For example, polyester composites with chopped-strand mat have impact strengths from 45 to 70 ft-lbf/in² (94–147 kJ/m²), whereas a typical impact strength for polyester resin is only about 1 ft-lbf/in² (2.1 kJ/m²).

The significant improvement in impact strength by reinforcement is explained by the energy required to cause debonding and to overcome friction in pulling the fibers out of the matrix. It follows from this that impact strengths would be higher if the bond between the fiber and the matrix is relatively weak, because if the interfacial bond is very strong, impact failure will occur by propagation of cracks across the matrix and fibers requiring very little energy.

It is also found that in short-fiber-reinforced plastics the impact strength is maximum when the fiber length has the critical value. The requirements for maximum impact strength (i.e., short fiber and relatively weak interfacial bond) are thus seen to be contrary to those for maximum tensile strength (long fibers and strong bond). The structure of a reinforced plastic material should therefore be tailored in accordance with the service conditions to be encountered by the material.

3.4 Electrical Properties

The usefulness of an insulator or dielectric ultimately depends on its ability to act as a separator for points across which a potential difference exists. This ability depends on the dielectric strength of the material, which is defined as the maximum voltage gradient that the material withstands before failure or loss of the material's insulating properties occurs.

Besides permittivity (dielectric constant), dielectric losses, and dielectric strength, another property used to define the dielectric behavior of a material is the insulation resistance, i.e., the resistance offered by the material to the passage of electric current. This property may be important in almost all applications of insulators.

This resistivity (i.e., reciprocal of conductivity) of a plastic material with a perfect structure would tend to be infinite at low electric fields. However, the various types of defects which occur in plastics may acts as sources of electrons or ions which are free to contribute to the conductivity or that can be thermally activated to do so. These defects may be impurities, discontinuities in the structure, and interfaces between crystallites and between crystalline and amorphous phases. Common plastics therefore have finite, though very high, resistivities from 10^8 to 10^{20} ohm-cm. These resistivity values qualify them as electrical insulators.

Polymeric materials have also been produced which have relatively large conductivities and behave in some cases like semiconductors and even photoconductors [28]. For example, polyphenylacetylene, polyaminoquinones, and polyacenequinone radical polymers have been reported with resistivities from 10^3 to 10^8 ohm-cm. It has been suggested that the conductivity in these organic semiconductors is due to the existence of large number of unpaired electrons, which are free within a given molecule and contribute to the conduction current by hopping (tunneling) from one molecule to an adjacent one (see Electroactive Polymers in [Chapter 5](#)).

3.4.1 Dielectric Strength

Dielectric strength is calculated as the maximum voltage gradient that an insulator can withstand before puncture or failure occurs. It is expressed as volts (V) per unit of thickness, usually per mil (1 mil = 1/1,000 in.).

Puncture of an insulator under an applied voltage gradient results from small electric leakage currents which pass through the insulator due to the presence of various types of defects in the material. (Note that only a perfect insulator would be completely free from such leakage currents.) The leakage currents warm the material locally, causing the passage of a greater current and greater localized warming of the material, eventually leading to the failure of the material. The failure may be a simple puncture in the area where material has volatilized and escaped, or it may be a conducting carbonized path (tracking) that short circuits the electrodes.

It is obvious from the cause of dielectric failure that the measured values of dielectric strength will depend on the magnitude of the applied electric field and on the time of exposure to the field. Since the probability of a flaw and a local leakage current leading ultimately to failure increases with the thickness of the sample, dielectric strength will also be expected to depend on the sample thickness.

The measurement of dielectric strength (Figure 3.52a) is usually carried out either by the short-time method or by the step-by-step method. In the former method the voltage is increased continuously at a uniform rate (500 V/sec) until failure occurs. Typically, a 1/8-in. thick specimen requiring a voltage of about 50,000 V for dielectric failure will thus involve a testing period of 100 sec or so.

In step-by-step testing, definite voltages are applied to the sample for a definite time (1 min), starting with a value that is half of that obtained by short-time testing, with equal increments of 2,000 V until failure occurs. Since step-by-step testing provides longer exposure to the electric field, dielectric strength values obtained by this method are lower than those obtained by the short-time test. Conditions to step-by-step testing correspond more nearly with those met in service. Even so, service failure almost invariably occurs at voltages below the measure dielectric strength. It is thus necessary to employ a proper safety factor to provide for the discrepancy between test and service conditions.

Increase in thickness increases the voltage required to give the same voltage gradient, but the probability of a flaw and a local leakage current leading ultimately to failure also increases.

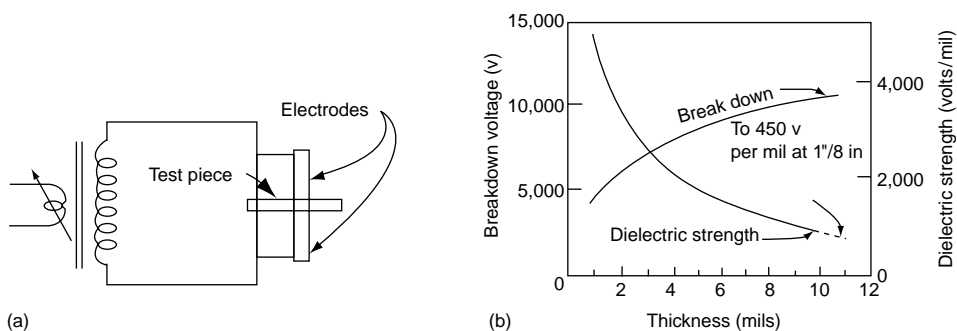


FIGURE 3.52 (a) Dielectric strength test. (b) Dependence of dielectric strength on thickness of sample.

The breakdown voltage increases proportionally less than thickness increases, and as a result the dielectric strength of a material decreases with the thickness of specimen (Figure 3.52b). For this reason, testing of insulation plastic should be done with approximately the thickness in which it is to be used in service.

It is seen from Figure 3.52b that the dielectric strength increases rapidly with decreasing thickness of the sample. A rule of thumb is that the dielectric strength varies inversely with the 0.4 power of the thickness. For example, if the dielectric strength of poly(vinyl chloride) plastic is 375 V/mil in a thickness of 0.075 in., it would be $375(75/15)^{0.4}$ or about 700 V/mil in foils only 15 mils thick. The fact that thin foils may have proportionally higher dielectric strength is utilized in the insulation between layers of transformer turns.

The dielectric strength of an insulation material usually decreases with increase in temperature and is approximately inversely proportional to the absolute temperature. But the converse is not observed, and below room temperature dielectric strength is substantially independent of temperature change.

Mechanical loading has a pronounced effect on dielectric strength. Since a mechanical stress may introduce internal flaws which serve as leakage paths, mechanically loaded insulators may show substantially reduced values of dielectric strength. Reductions up to 90% have been observed.

Dielectric strength of an insulating material is influenced by the fabrication detail. For example, flow lines in a compression molding or weld lines in an injection molding may serve as paths of least resistance for leakage currents, thus reducing the dielectric strength. Even nearly invisible minute flaws in a plastic insulator may reduce the dielectric strength to one-third its normal value.

3.4.2 Insulation Resistance

The resistance offered by an insulating material to the electric current is the composite effect of volume and surface resistances, which always act in parallel. Volume resistance is the resistance to leakage of the electric current through the body of the material. It depends largely on the nature of the material. But surface resistance, which is the resistance to leakage along the surface of a material, is largely a function of surface finish and cleanliness. Surface resistance is reduced by oil or moisture on the surface and by surface roughness. On the other hand, a very smooth or polished surface gives greater surface resistance.

A three-electrode system, as shown in Figure 3.53, is used for measurement of insulation resistance. In this way the surface and volume leakage currents are separated. The applied voltage must be well below the dielectric strength of the material. Thus, in practice, a voltage gradient less than 30 V/mil is applied. From the applied voltage and the leakage current, the leakage resistance is computed. Since the measured

value depends, among other things, on the time during which the voltage is applied, it is essential to follow a standardized technique, including preconditioning of the specimen to obtain consistent results.

The insulation resistance of a dielectric is represented by its volume resistivity and surface resistivity. The volume resistivity (also known as specific volume resistance) is defined as the resistance between two electrodes covering opposite faces of a centimeter cube. The range of volume resistivities of different materials including plastics is shown in Figure 3.54. Values for plastics range from approximately 10^{10} ohm-cm for a typical cellulose acetate to about 10^{19} ohm-cm for a high-performance polystyrene.

The surface resistivity (also known as specific surface resistance) is defined as the resistance measured between the opposite edges of the

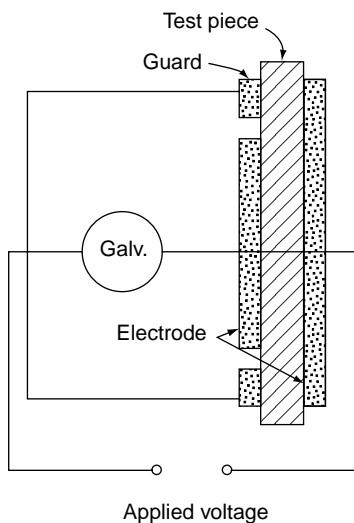


FIGURE 3.53 Insulation resistance test.

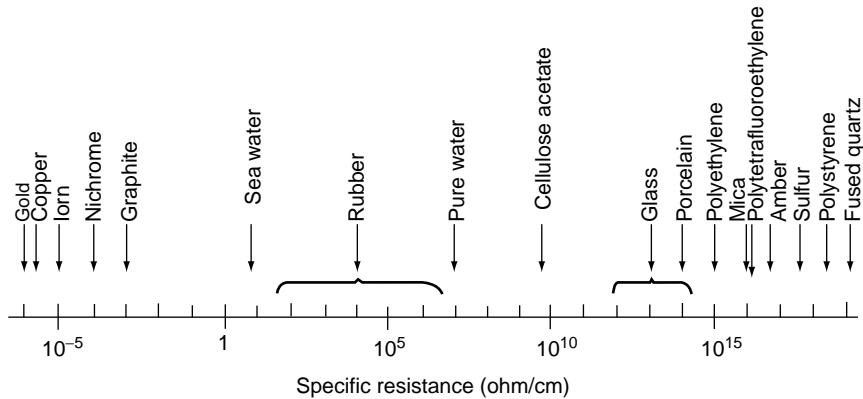


FIGURE 3.54 The resistivity spectrum.

surface of a material having an area of 1 cm^2 . It ranges from 10^{10} ohm for cellulose acetate to 10^{14} ohm for polystyrene.

The insulation resistance of most plastic insulating materials is affected by temperature and the relative humidity of the atmosphere. The insulation resistance falls off appreciably with an increase in temperature or humidity. Even polystyrene, which has very high insulation resistance at room temperature, becomes generally unsatisfactory above 80°C (176°F). Under these conditions polymers like polytetrafluoroethylene and polychlorotrifluoroethylene are more suitable. Plastics that have high water resistance are relatively less affected by high humidities.

3.4.3 Arc Resistance

The arc resistance of a plastic is its ability to withstand the action of an electric arc tending to form a conducting path across the surface. In applications where the material is subject to arcing, such as switches, contact bushes, and circuit breakers, resistance to arc is an important requirement. Arcing tends to produce a conducting carbonized path on the surface.

The arc resistance of an insulator may be defined as the time in seconds that an arc may play across the surface without burning a conducting path. A schematic of an arc-resistance test is shown in Figure 3.55.

Plastics that carbonize easily (such as phenolics) have relatively poor arc resistance. On the other hand, there are plastics (such as methacrylates) that do not carbonize, although they would decompose and give off combustible gases. There would thus be no failure in the usual sense. Special arc-resistant

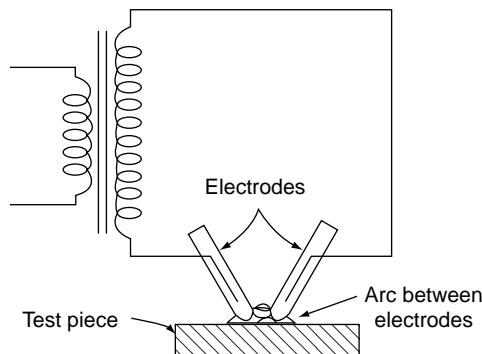


FIGURE 3.55 Arc-resistance test.

formulations involving noncarbonizing mineral fillers are useful for certain applications. But when service conditions are severe in this respect, ceramics ought to be used, because they generally have much better arc resistance than organic plastics.

Related to arc resistance is ozone resistance. This gas is found in the atmosphere around high-voltage equipment. Ignition cable insulation, for example, should be ozone resistant. Natural rubber is easily attacked and deteriorated by ozone. Fortunately, most synthetic resins have good ozone resistance and are satisfactory from this point of view.

3.4.4 Dielectric Constant

The effect of a dielectric material in increasing the charge storing capacity of a capacitor can be understood by considering the parallel-plate type sketched in Figure 3.56. If a voltage V is applied across two metal plates, each of area $A \text{ m}^2$, separated by a distance, $d \text{ m}$, and held parallel to each other in vacuum, the electric field established between the plates (Figure 3.56a) is

$$E = \frac{-V}{d} \quad (3.145)$$

The charge density, Q_0/A , where Q_0 is the total charge produced on the surface area A of each plate, is directly proportional to the electric field.

$$\frac{Q_0}{A} = -\epsilon_0 E = \epsilon_0 \frac{V}{d} \quad (3.146)$$

or

$$Q_0 = \frac{A\epsilon_0}{d} V = C_0 V \quad (3.147)$$

The proportionality constant, ϵ_0 , is called the dielectric constant (or permittivity) of a vacuum. It has units of

$$\epsilon_0 = \frac{Q_0/A}{V/d} = \frac{\text{coul}/\text{m}^2}{\text{V}/\text{m}} = \frac{\text{coul}/\text{V}}{\text{m}} = \frac{\text{farad}}{\text{m}}$$

and a value of $8.854 \times 10^{-12} \text{ farad}/\text{m}$.

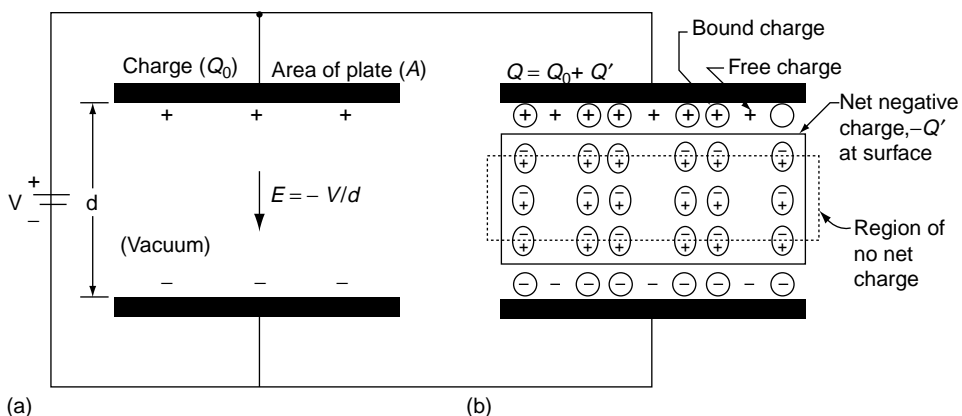


FIGURE 3.56 Schematic illustration of the effect of dielectric material in increasing the charge storing capacity of a capacitor.

The quantity C_0 in Equation 3.147 is the capacitance of a capacitor (condenser) with a vacuum between its plates. It can be defined as the ratio of the charge on either of the plates to the potential differences between the plates.

Now if a sheet of a dielectric material is inserted between the plates of a capacitor (Figure 3.56b), an increased charge appears on the plates for the same voltage, due to polarization of the dielectric. The applied field E causes polarization of the entire volume of the dielectric and thus gives rise to induced charges, or bound charges, Q' , at its surface, represented by the ends of the dipole chains. These induced charges may be pictured as neutralizing equal charges of opposite signs on the metal plates. If one assumes, for instance, that the induced charge $-Q'$ neutralizes an equal positive charge in the upper plate of the capacitor (Figure 3.56b), the total charge stored in the presence of the dielectric is $Q = Q_0 + Q'$.

The ratio of the total charge Q to the free charge Q_0 (which is not neutralized by polarization) is called the relative dielectric constant or *relative permittivity*, ϵ_r , and is characteristic of the dielectric material.

$$\epsilon_r = \frac{\text{Total charge}}{\text{Free charge}} = \frac{Q}{Q_0} \quad (3.148)$$

Obviously, ϵ_r is always greater than unity and has no dimensions. For most materials ϵ_r exceeds 2 (Table 3.6).

Dividing both the numerator and denominator of Equation 3.148 by the applied voltage V and applying the definition of C from Equation 3.147, we obtain

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} = \frac{C}{C_0} \quad (3.149)$$

The relative dielectric constant or relative permittivity is thus defined as the ratio of the capacitance of a condenser with the given material as the dielectric to that of the same condenser without the dielectric. (The dielectric constant for air is 1.0006. It is usually taken as unity—that is, the same as a vacuum—and the relative dielectric constant is referred to simply as the dielectric constant).

TABLE 3.6 Dielectric Properties of Electrical Insulators

Material	ϵ_r at 60 Hz	$\tan \delta$		Dielectirc Strength ^a (V/mil)
		60 Hz	10 ⁶ Hz	
<i>Ceramics</i>				
Porcelain	6	0.010	—	—
Alumina	9.6	—	<0.0005	200–300
Zircon	9.2	0.035	0.001	60–290
Soda-lime	7	0.1	0.01	—
Fused silica	4	0.001	0.0001	—
Mica	7	—	0.0002	3,000–6,000 (1–3 mil specimen)
<i>Polymers</i>				
Polyethylene	2.3	<0.0005	—	450–1,000
Polystyrene	2.5	0.0002	0.0003	300–1,000
Polyvinyl chloride	7	0.1	—	300–1,000
Nylon-6, 6	4	0.02	0.03	300–400
Teflon	2.1	<0.0001	—	400

^a Specimen thickness 1/8 in.

The dielectric susceptibility, χ , is defined as

$$\chi = \epsilon_r - 1 = \frac{\epsilon - \epsilon_0}{\epsilon_0} \quad (3.150)$$

It thus represents the part of the total dielectric constant which is a consequence of the material. From Equation 3.148,

$$\chi = \frac{\text{Bound charge}}{\text{Free charge}}$$

The magnitude of the induced or bound charge Q' per unit area is the polarization, P , which has the same units as charge density.

Therefore,

$$P = \frac{Q'}{A} = \frac{Q - Q_0}{A} \quad (3.151)$$

Substituting from Equation 3.146, Equation 3.148, and Equation 3.150, we obtain

$$P = \chi \epsilon_0 E = \epsilon_0 (\epsilon_r - 1) E \quad (3.152)$$

This equation, as we shall see later, provides a link between the permittivity, which is a macroscopic, measurable property of a dielectric, and the atomic or molecular mechanisms in the dielectric which give rise to this property.

3.4.4.1 Polarization and Dipole Moment

In terms of the wave-mechanical picture, an atom may be looked upon as consisting of a positively charged nucleus surrounded by a negatively charged cloud, which is made up of contribution from electrons in various orbitals. Since the centers of positive and negative charges are coincident (see Figure 3.57a), the net dipole moment of the atom is zero.

If an electric field is applied, however, the electron cloud will be attracted by the positive plate and the nucleus by the negative plate, with the result that there will occur a small displacement of the center of gravity of the negative charge relative to that of the positive charge (Figure 3.57a). The phenomenon is described by the statement that the field has induced an electric dipole in the atom; and the atom is said to have suffered electronic polarization—electronic because it arises from the displacement of the electron cloud relative to the nucleus.

The electric dipole moment of two equal but opposite charges, $+q$ and $-q$, at a distance r apart is defined as qr . For the atomic model of Figure 3.57a, it can be shown by balancing the opposite forces of the electric field and the coulombic attraction between the nucleus and the center of the electron cloud that the dipole moment, μ , induced in an atom by the field E is

$$\mu = (4\pi\epsilon_0 R^3)E = \alpha_e E \quad (3.153)$$

where α_e is a constant, called the electronic polarizability of the atom. It is proportional to the volume of the electron cloud, R^3 . thus the polarizability increases as the atoms become larger.

On the macroscopic scale we have earlier defined the polarization, P , to represent the bound charges induced per unit area on the surface of the material. Therefore, if we take unit areas on opposite faces of a cube separated by a distance d , the dipole moment due to unit area will be

$$\mu = Pd$$

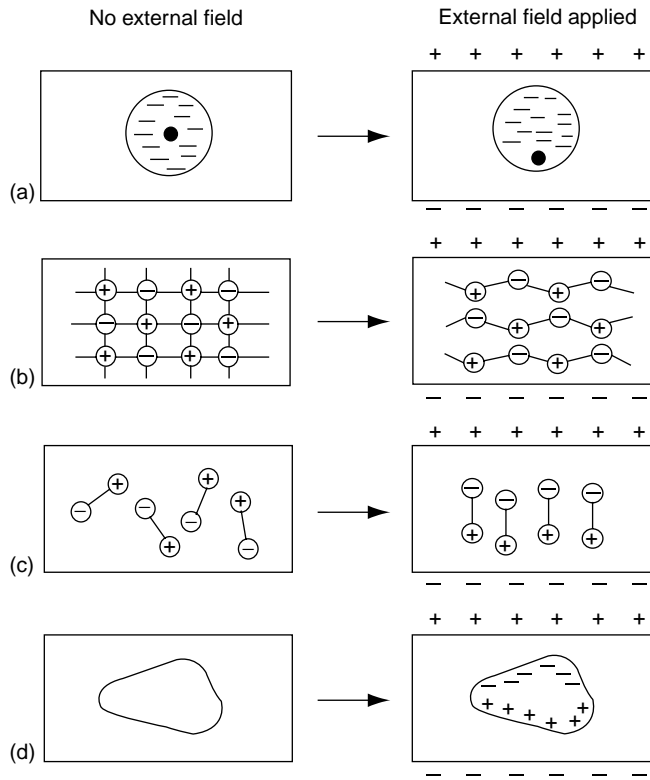


FIGURE 3.57 Schematic illustrations of polarization mechanisms. (a) Electronic displacement. (b) Ionic displacement. (c) Dipole orientation. (d) Space charge.

For $d=1$ (i.e., for unit volume) $\mu=P$. The polarization P is thus identical with the dipole moment per unit volume (check the units: coul/m²=coul m/m³).

A dipole moment may rise through a variety of mechanisms, any or all of which may thus contribute to the value of P . The total polarization may be represented as a sum of individual polarizations, each arising from one particular mechanism (Figure 3.57) or, more appropriately, as an integrated sum of all the individual dipole moments per unit volume.

$$P = P_e + P_i + P_0 + P_s = \frac{\sum \mu_e + \sum \mu_i + \sum \mu_0 + \sum \mu_s}{V} \quad (3.154)$$

Electronic polarization, P_e , as discussed previously, arises from electron displacement within atoms or ions in an electric field; it occurs in all dielectrics. Similarly, displacements of ions and atoms within molecules and crystal structures (Figure 3.57b) under an applied electric field give rise to ionic (or atomic) polarization, P_i . Orientation polarization, P_0 , arises when asymmetric (polar) molecules having permanent dipole moments are present, since they become preferentially oriented by an electric field (Figure 3.57c). Interfacial (or space charge) polarization, P_s , is the result of the presence of higher conductivity phases in the insulating matrix of a dielectric, causing localized accumulation of charge under the influence of an electric field (Figure 3.57d).

Any or all of these mechanisms may be operative in any material to contribute to its polarization. A question to be discussed now is, which of the mechanisms are important in any given dielectric? The answer lies in studying the frequency dependence of the dielectric constant.

3.4.4.2 Dielectric Constant versus Frequency

Let us consider first a single dipole in an electric field. Given time, the dipole will line up with its axis parallel to the field (Figure 3.57c). If now the field is reversed, the dipole will turn 180° to again lie parallel to the field, but it will take a finite time; so if the frequency of the field reversal increases, a point will be reached when the dipole cannot keep up with the field, and the alteration of the dipole direction lags behind that of the field. For an assembly of dipoles in a dielectric, this condition results in an apparent reduction in the dielectric constant of the material. As the frequency of the field continues to increase, at some stage the dipoles will barely have started to move before the field reverses. Beyond this frequency, called the relaxation frequency, the dipoles make virtually no contribution to the polarization of the dielectric.

We may now consider the various mechanisms and predict, in a general way, the relaxation frequency for each one. Electrons with their extremely small mass have little inertia and can follow alterations of the electric field up to very high frequencies. Relaxation of electronic polarization is thus not observed until about 10^6 Hz (ultraviolet region). Atoms or ions vibrate with thermal energy, and the frequencies of these vibrations correspond to the infrared frequencies of the electromagnetic spectrum. The relaxation frequencies for ionic polarization are thus in the infrared range.

Molecules or groups of atoms (ions) behaving as permanent dipoles may have considerable inertia, so relaxation frequencies for orientation polarization may be expected to occur at relatively smaller frequencies, as in the radio-frequency range. Since the alternation of interfacial polarization requires a whole body of charge to be moved through a resistive material, the process may be slow. The relaxation frequency for this mechanism is thus low, occurring at about 10^3 Hz.

Figure 3.58 shows a curve of the variation of the dielectric constant (relative permittivity) with frequency for a hypothetical solid dielectric having all four mechanisms of polarization. Note that except at high frequencies the electronic mechanism makes a relatively low contribution to permittivity. However, in the optical range of frequencies, only this mechanism and the ionic mechanism operate; they therefore strongly influence the optical properties of materials.

3.4.4.3 Dielectric Constant versus Temperature

Liquids have higher dielectric constants than solids because dipole orientation is easier in the former. The effect is shown schematically in Figure 3.59a. After the abrupt change due to melting, the dielectric

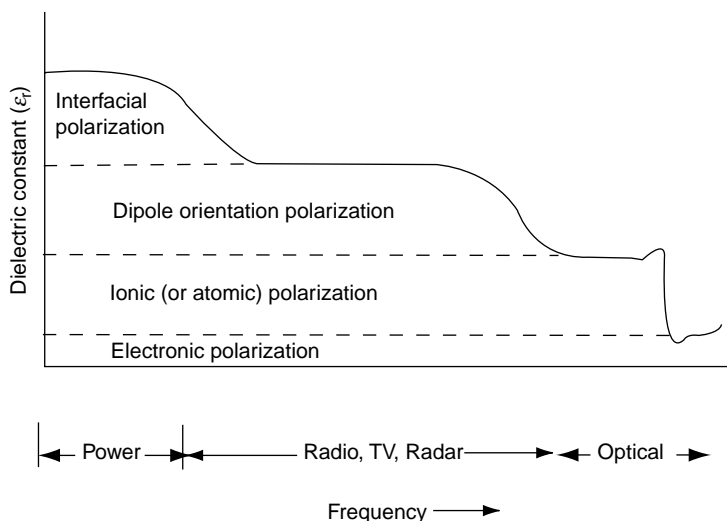


FIGURE 3.58 Dielectric constant versus frequency.

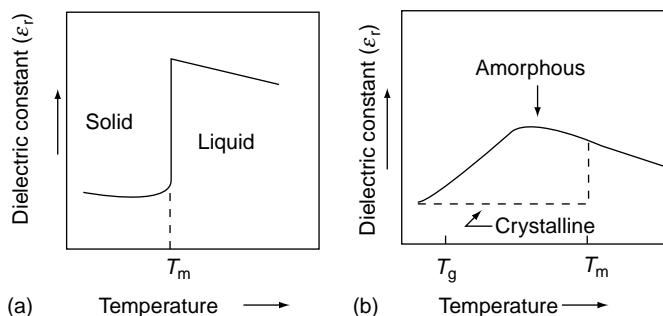


FIGURE 3.59 Variation of dielectric constant with temperature (schematic). (a) Crystalline material. (b) Amorphous polymer. A crystalline polymer containing polar group would behave as shown by dashed lines.

constant decreases as the temperature is increased, which is due to the higher atomic or molecular mobility and thermal collisions tending to destroy the orientation of dipoles.

Figure 3.59b shows the schematic variations of dielectric constants with temperature for amorphous solids, such as glasses and many polymers. Above the glass transition temperature (T_g), atoms and molecules have some freedom of movement, which allows orientation of permanent dipoles with the field, thereby increasing the dielectric constant. Since the polar groups which contribute to orientation polarization are not identically situated in an amorphous matrix, the dielectric constant changes over a temperature range rather than abruptly at a single temperature as in a crystalline material (cf. Figure 3.59a). The decrease in the dielectric constant after melting is again due to greater molecular mobility and thermal collisions.

3.4.4.4 Dielectric Losses

The behavior of a dielectric under an applied field has much in common with that of a material subjected to mechanical loading. The displacements of atoms and molecules within a material, when a mechanical force is applied, do not occur instantaneously but lag behind the force, resulting in elastic aftereffect and energy dissipation by mechanical hysteresis under an alternating force. Similarly, in dielectrics the lag of polarization behind the applied field produces energy dissipation by electrical hysteresis in an alternating field (Figure 3.60b). Such energy losses are related to the internal dipole friction. The rotation of dipoles with the field is opposed by the internal friction of the material, and the energy required to maintain this rotation contributes to the power loss in dielectrics.

Besides electrical hysteresis, leakage currents also contribute to dielectric losses. Leakage currents occur mainly by ionic conduction through the dielectric material and are usually negligible except at high temperatures. There are various ways of measuring energy losses by a dielectric.

A fundamental property of a capacitor is that if an alternating voltage is applied across it in a vacuum, the current that flows to and from it due to its successive charging and discharging is 90° out of phase with the voltage (Figure 3.60c), and no energy is lost. However, in real capacitors containing a dielectric, the lag of polarization causes a phase shift of the current (Figure 3.60d). The phase shift angle, δ , is called the loss angle, and its tangent ($\tan \delta$) is referred to as the loss tangent or dissipation factor. (An ideal dielectric would have a phase angle of 90° , and hence the loss angle would be zero.)

The sine of the loss angle ($\sin \delta$) or the cosine of the phase angle ($\cos \theta$) is termed the power factor. In electrical applications the power loss (PL) is defined as the rate of energy loss per unit volume and is derived to be

$$PL = \frac{\omega E^2 \epsilon_0}{2} \epsilon_r \tan \delta \quad (3.155)$$

where E is the electric field and ω is the angular velocity; $\epsilon_r \tan \delta$ is called the *loss factor*.

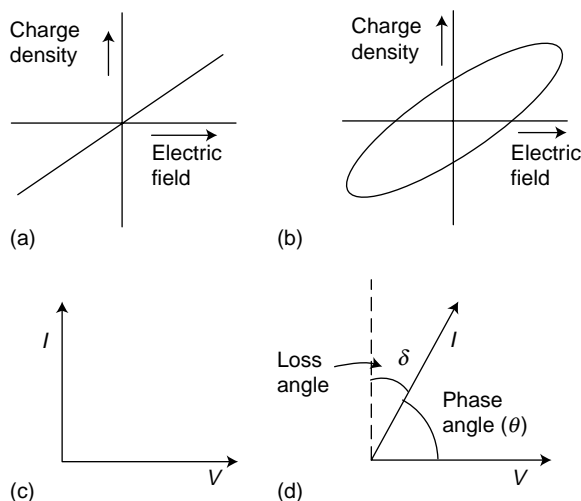


FIGURE 3.60 Charge density versus electric field. (a) Loss-free cycle. (b) High-loss cycle. (c) Phase shift in a perfect capacitor. (d) Phase shift in a real capacitor.

For most materials δ is very small; consequently, the three measures of energy dissipation— δ , $\tan \delta$, and $\sin \delta (= \cos \theta)$ —are all approximately the same. Since these values vary somewhat with frequency, the frequency must be specified (see Table 3.6).

It is evident from this discussion that the power loss and heat dissipation in a dielectric will be aided by a high dielectric constant, high dissipation factor, and high frequency. Therefore, for satisfactory performance electrical insulating materials should have a low dielectric constant and a low dissipation factor but a high dielectric strength (Table 3.6) and a high insulation resistance.

Polyethylene and polystyrene with their exceptionally low dissipation factors (<0.0005) and low dielectric constant (2.3–2.5) are the most suitable for high-frequency applications, as in television and radar. For dielectrics used in capacitors, however, a high dielectric constant is desirable.

3.4.4.5 Dielectric Losses of Polar Polymers

When a polymer having polar groups (e.g., polymethyl methacrylate, polyvinyl chloride) is placed in an electric field, the polar groups behaving as dipoles tend to orient themselves in response to the field (Figure 3.61a). In an alternating field the friction of the dipoles rotating with the field contributes to the dielectric loss. This loss is small at low frequencies where the polar groups are able to respond easily to the field, and also at high frequencies where the polar groups are unable to change their alignment with the field. The loss is maximum in the transitional region where the polymer is passing from high response at low frequency to low response at high frequency (Figure 3.61b).

Since the friction of dipoles in an alternating field produces heat, polar polymers can be heated by the application of radio-frequency field in fabrication processes (see high-frequency welding, Chapter 2).

3.5 Optical Properties

Optical characteristics of plastics include color, clarity, general appearance, and more directly measurable properties, such as index of refraction [29]. For optical applications, however, other properties, including dimensional stability, scratch resistance, temperature limitation, weatherability, and water absorption, must be considered.

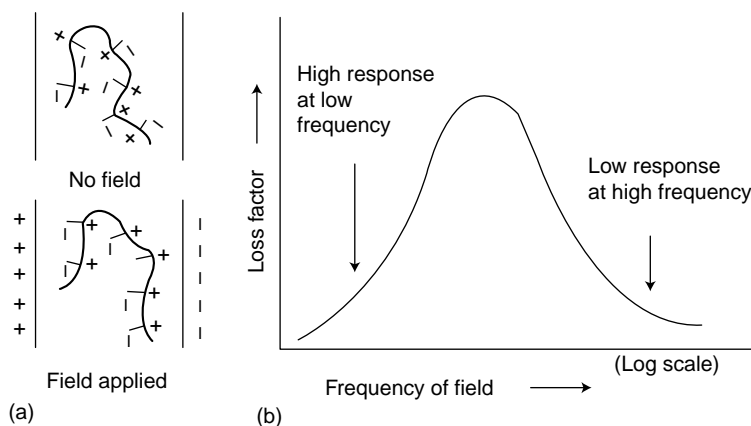


FIGURE 3.61 (a) Orientation of a polar polymer molecule in an electric field. (b) Dielectric response of a polar polymer in an alternating electric field.

3.5.1 Optical Clarity

Most resins by nature are clear and transparent. They can be colored by dyes and will become opaque as pigments or fillers are added. Polystyrene and poly (methyl methacrylate) are well known for their optical clarity, which even exceeds that of most glass. Optical clarity is a measure of the light transmitting ability of the material. It depends, among other things, on the length of the light path, which can be quantitatively expressed by the Lambert-Beer law, or $\log (I/I_0) = -AL$, where I/I_0 is the fraction of light transmitted, L is the path length, and A is the absorptivity of the material at that wavelength. The absorptivity describes the effect of path length and has the dimension of reciprocal length.

Transparent colored materials are obtained by adding a dye to a water white resin. A color results when a dye removes part of the visible light traveling through the piece. The red color, for example, is produced by a dye which absorbs the blue, green, and yellow components of the light and transmits the red unchanged (Figure 3.62). However, for any dye to be effective it must be soluble in the plastic, and it is best incorporated in the plastic before molding. Fluorescent dyes absorb radiant energy at one wavelength, perhaps in the ultraviolet, and emit it as less energetic but more visible radiation.

Cast phenolics, allyls, cellulotics, and many other clear plastics show a natural tendency to absorb in the blue and to be yellowish. Ultraviolet photodecomposition is largely responsible for the development of

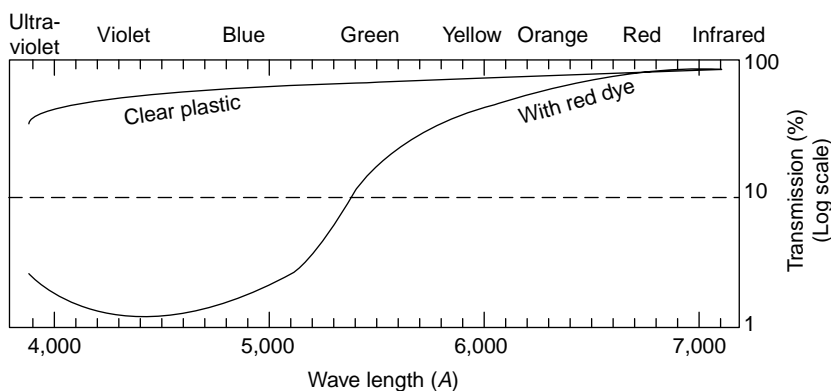


FIGURE 3.62 Light transmission diagram for plastic.

yellowish color in plastics exposed to sunlight. Incorporation of an invisible ultraviolet-absorbing material such as phenyl salicylate or dihydroxybenzophenone in the plastic greatly reduces photodecomposition.

Addition of a blue or green tint into the plastic can also mask the yellow color. In addition to yellowing, plastics show darkening due to outdoor exposure as the transmission curve shifts downward, and there is pronounced absorption at wavelengths shorter than about 5,000 Å (Figure 3.63).

The optical clarity of a plastics specimen is measured by the lack of optical haze. Haze is arbitrarily defined as the fraction of transmitted light which is deviated $2\frac{1}{2}^\circ$ or more from an incident beam by forward scattering. When the haze value is greater than 30%, the material is considered to be translucent. The forward scattering of the light beam, which is responsible for haze, occurs at internal interfaces such as caused by a dust particle, bubble, particles of a filler or pigment, or by density changes.

Due to scattering at interfaces, a crystalline plastic with myriads of crystallite regions bounded by interfaces is translucent. Crystalline polyethylene is thus translucent at room temperature, but, on warming, the crystallites disappear and the material becomes transparent. It can thus be inferred that plastics which are transparent at room temperature, such as polystyrene or poly(methyl methacrylate), are of the noncrystalline type and without fillers.

The effect of interfaces due to fillers depends to a large extent on the difference in the indices of refraction of plastic and filler. Thus transparent glass-filled polyester panels are obtained if the indices of refraction of glass and resin are identical and the glass is surface treated to enable the resin to wet the glass completely.

3.5.2 Index of Refraction

The index of refraction for any transparent material is the ratio of the sine of the angle of an incident ray to the sine of the angle of refraction (Figure 3.64). It also corresponds to the ratio of the speed of light in a vacuum (or air, closely) to its speed in the material. The refractive index values of several common plastics are compared with those of other materials in Table 3.7.

The refraction property makes possible the focusing action of a lens. Plastic lenses have the advantage that they are light in weight (about half as heavy as glass) and practically nonshattering. But they have the disadvantage of low scratch resistance and comparatively poor dimensional stability for temperature changes.

When tolerances are less critical, plastic lenses can be mass produced by virtue of the moldability of plastics; these lenses are quite satisfactory for inexpensive camera view finders, for example, but in applications where exacting tolerances are required, such as cameras, periscopes, or similar high-resolution devices, molded plastic lenses have not been suitable. If plastic lenses are to be used in these

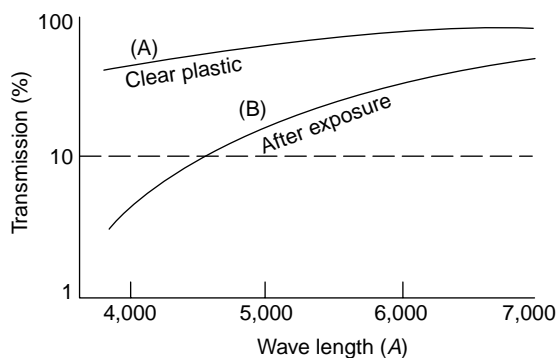


FIGURE 3.63 Yellowing of plastics on exposure.

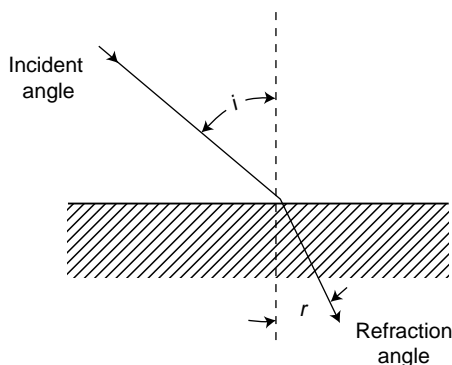


FIGURE 3.64 Refraction of light. Index of refraction: $n = (\sin i)/(\sin r)$.

applications, they should be ground and polished in much the same manner as in glass, though, of course, it is easier to do so (Figure 3.65).

The refractive index, n , of an isotropic material is given by the Lorentz–Lorenz relation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi P$$

where P is the optical polarizability per unit volume of material. For a pure substance it is more convenient to write this equation in the form

$$\frac{(n^2 - 1)M}{(n^2 + 2)\rho} = \frac{4}{3} \pi N_A \alpha = R \quad (3.156)$$

where M is the molecular weight of the substance, ρ is the density, N_A is Avogadro's number, α is the optical polarizability of a single molecule of the substance, and R is the molar refraction.

The quantity α represents the amount of polarization of the molecule per unit electric field caused by the alternating electric field associated with the light ray passing through the material. The polarization may be regarded as due to the shift of the center of charge of the more loosely bound electrons relative to the nucleus (see Figure 3.57).

The refractive index varies with wavelength of light and is measured by the optical dispersion—that is, the difference in the refractive indexes for different wavelengths. It is responsible for the spectrum-separating ability of a prism in a spectroscope. Most plastics have relatively low optical dispersion. This property makes them more suitable for eyeglasses and large lenses for projection television.

3.5.3 Piped Lighting Effect

The difference in indexes of refraction for air and for a transparent solid (plastic or glass) is responsible for the ability of the latter, used as a rod or plate, to bend or pipe light around a curve. Bending can be explained as follows. It is evident from Figure 3.64 that a light beam in air cannot enter a material with $i > 90^\circ$. Since $\sin 90^\circ = 1$, the maximum angle of refraction is that for which the sine is $1/n$, where n is the index of refraction. For poly(methyl methacrylate) $n = 1.49$, and the maximum angle of refraction becomes $\sin^{-1}(1/1.49)$ or 42° approximately. Obviously a light beam refracted at a greater angle cannot have come from the air, but it must have been reflected internally. A plastic plate with small curvature therefore gives internal reflections and can thus bend a light beam, as shown in Figure 3.65.

TABLE 3.7 Index of Refraction

Material	Index of Refraction (n)
Air	1.00
Water	1.33
Cellulose acetate	1.48
Poly(methyl methacrylate)	1.49
Common glass	1.52
Poly(vinyl chloride) copolymer	1.53
Polystyrene	1.59
Flint glass	1.65
Diamond	2.42

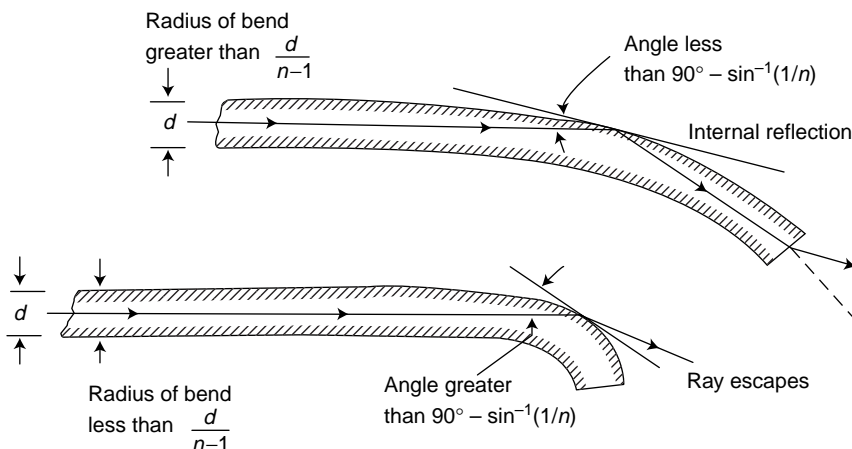


FIGURE 3.65 Principle of piped light.

Consideration of geometric optics shows the minimum radius of curvature for this piping of light to correspond to $1/(n-1)$ times the thickness.

Polymer has numerous advantages over glass [30]. First and foremost, it is more pliable. It is also nonshattering, lightweight, and easy to fabricate. Polymer optical fiber (POF) has a shorter bend radius (i.e., more flexibility) and is more resilient to damage and abuse than glass due to its intrinsic material characteristics. The bending radius depends largely on the diameter of the fiber, large fiber giving a larger bend radius. Thus, for an outside diameter of one millimeter ($1,000\ \mu\text{m}$), the bend radius (damage threshold) is approximately one centimeter, while for single-mode POF with outside diameter of $125\ \mu\text{m}$, the bend radius is as low as $0.125\ \text{cm}$. The level of intensity loss from bending depends on the individual characteristics of the fiber, but intensity loss values have been observed at 10%–15% for bends close to the minimum (damage threshold) radius.

Attenuation is a measurement, in decibels (dB) per unit length, of how much reduction in light (due to absorption) is experienced per unit length of the fiber. Absorption varies largely with the wavelength of light. The attenuation of PMMA, generally used as POF core material, is approximately 100 dB/km in the visible region and increases rapidly at higher wavelength (Figure 3.66). This high attenuation of POF compared to the silica-based fiber limits the data link length. However, the field witnessed real progress in 1980s when low loss polymers were developed and drawn into fibers (see Chapter 5).

The light bending ability of POF is made use of in a wide variety of applications ranging from lighting scheme for pools and fountains to telecommunications and consumer electronics. In these applications (see more details in Chapter 5), the POF serves as a medium for transmitting light for illumination or imaging, or for transporting and/or controlling information that is encoded on a beam of light [31].

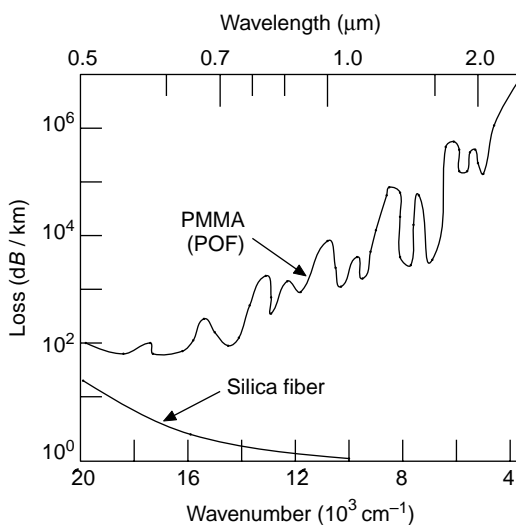


FIGURE 3.66 Variation of attenuation of PMMA and silica-based fibers with wavelength.

3.5.4 Stress-Optical Characteristics

An important phenomenon observed in amorphous plastics (also observed in optical glass) is the development of optical anisotropy due to stress. The stress-optical characteristic of transparent plastics is the basis of the important technique of photoelasticity by which stress and strain in complicated shapes, for which no analytical solution is readily available, can be determined experimentally and simply.

The amount of strain in various parts of a transparent plastic model of a machine part, subjected to loads simulating those in actual operation, is determined by measuring the anisotropy with polarized light; therefore from this measurement the distribution of stress and strain in the actual metal part can be deduced. Very complicated shapes, including complete structures such as bridges or aircraft wings, have been successfully analyzed in this manner, employing plastic models.

The same stress-optical characteristic also permits examination of locked-in stresses in a molded plastic part. The part is examined under polarized light, and the amount of stress is indicated by the number of fringes or rings that become visible. Illumination with white light gives colorful patterns involving all the colors of the spectrum. Monochromatic light is, however, used for stress analysis because it permits more precise measurements.

In general, a single ray of light entering an anisotropic transparent material, such as crystals of sufficiently low symmetry and strained or drawn polymers, is propagated as two separate rays which travel with different velocities and are polarized differently. Both the velocities and the state of polarization vary with the direction of propagation. This phenomenon is known as birefringence or double refraction, and the material is said to be birefringent.

The stress-optical characteristic of plastics arises from this phenomenon of birefringence, induced by strains due to applied stress. The applied stress produces different densities along different axes. The stress-optical coefficient of most plastics is about 1,000 psi (70 kgf/cm² or 6.9 Mpa) per inch (2.54 cm) thickness per fringe. This means that a 1-in. thick part when illuminated with monochromatic light and viewed through a polarizing filter will show a dark fringe or ring for a stress of 1,000 psi. This sensitivity is many times higher than that shown by glass and makes transparent plastics useful in photoelastic stress analysis.

In one variation of the process the deforming stress is applied to a warm, soft plastic model which is then quenched to room temperature. The resulting locked-in stress may then be analyzed at leisure or, perhaps more conveniently, by cutting sections from the model and examining them separately. For this application, however, the plastic should have stress-optical stability. In this regard, unplasticized transparent plastics such as poly(methyl methacrylate), polystyrene, and cast poly(allyl phthalate) are superior to plasticized materials such as cellulose acetate.

3.6 Thermal Properties

The useful thermal properties of plastics include specific heat, thermal expansion, thermal conductivity, and thermal softening [32].

3.6.1 Specific Heat

For most plastics the specific heat value (calories per gram per °C) lies between 0.3 and 0.4. On a weight basis this value is much higher than that of most metals. Both iron and copper, for example, have specific heats of about 0.1 at ordinary temperatures. However, along a volume basis, the specific heats of plastics are lower than those of common metals, because of the substantially lower density of plastics.

Knowledge of specific heat of a material helps to determine the energy requirement for increasing its temperature. In compression molding and injection molding the theoretical heat requirement can be calculated as the sum of this direct heat and any latent heat of melting minus any energy released by chemical reaction. But this heat requirement is not large compared to the heat loss by radiation and conduction from the press. The proportion of losses is substantially lower for injection molding than for

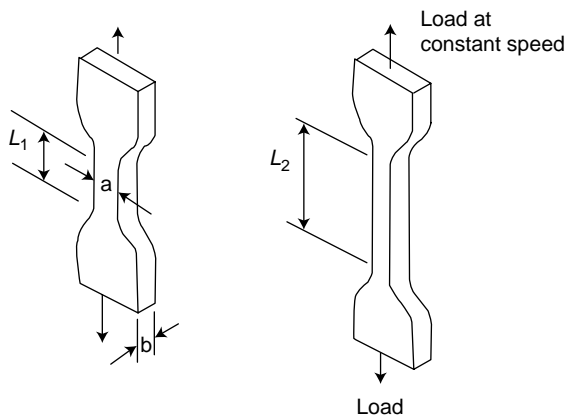


FIGURE 3.67 Tests for tensile strength (stress at fracture of the specimen) and elongation (extension of materials under load) of plastics. The first provides a measure of the breaking strength of the material but is radically affected by the rate of loading and the ambient temperature. Tensile strength in lbf/in.^2 or $\text{kgf/cm}^2 = \text{load (lbf or kgf)} / a \times b$ (in.^2 or cm^2). Standard test methods: BS 2782 method 301, ASTM D638, ISO R527. Elongation $\% = (L_2 - L_1) \times 100 / L_1$. Standard test methods: BS 2782 method 301, ASTM D638.

compression molding. It is nevertheless customary in both cases to establish the heating requirements as well as mold cooling requirements by a process of trial and error.

In dielectric preheating, however, the specific heat of a molding powder is of more direct concern; this knowledge along with the amount of material and time enables one to calculate the required amount of radio-frequency power. For example, to raise the temperature of a 1-kg perform of specific heat 0.35 through 80°C in 1 min requires $1 \times 0.35 \times 80$ or 28 kcal/min or about 2 kW.

3.6.2 Thermal Expansion

Linear (thermoplastic) polymers have very high thermal expansion coefficients since they are weakly bonded materials and need less input of thermal energy to expand the structure. This applies to all polymers of the vinyl type which have expansion coefficients of about $90 \times 10^{-6}/^\circ\text{C}$. Network (thermosetting) polymers having a three-dimensional framework of strong covalent bonds exhibit less thermal expansion and have expansion coefficients in the range of $30\text{--}70 \times 10^{-6}/^\circ\text{C}$. These may be

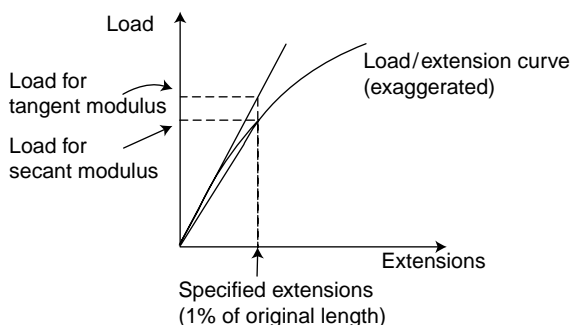


FIGURE 3.68 Test for tangent and secant moduli of plastics. For tangent modulus, load on tangent to load-extension curve at specified extension is used for calculating the stress value, while for secant modulus load on secant to load-extension curve is used. The modulus is given by stress/strain. Standard test methods: BS 2782 method 302, ASTM D638, ISO R527.

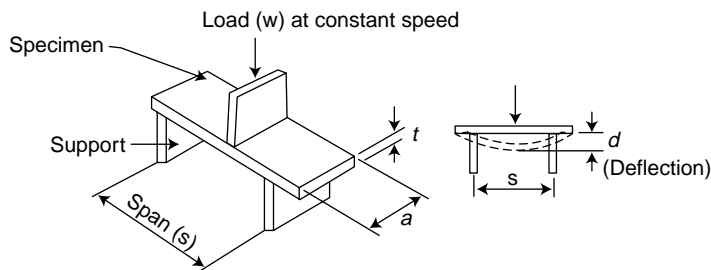


FIGURE 3.69 Tests for flexural properties of plastics. Flexural strength $= 3ws/2at$ (lbf/in.² or kgf/cm²). Standard test method: ASTM D790. Modulus in flexure $= s^3w/4at^3d$ (lbf/in.² or kgf/cm²). Standard test methods: BS 2782 method 302D, ASTM D790, ISO R178.

compared with values of $11 \times 10^{-6}/^{\circ}\text{C}$ for mild steel, $17 \times 10^{-6}/^{\circ}\text{C}$ for ordinary brass, and less than $10 \times 10^{-6}/^{\circ}\text{C}$ for ceramics. In spite of high thermal expansion, plastics do not easily undergo thermal cracking, because they also have very low elastic moduli and large strains do not induce high stresses.

One area where the high expansion of polymers plays a significant role is the molded dimensions of plastic parts. The linear mold shrinkage due to thermal contraction from molding to room temperature is usually about 1/2%–1%. Polyethylene and certain other materials exhibit even a higher shrinkage. As a result, plastic parts with close tolerances are difficult to make. It is also possible during the molding operation that different parts are not all at a uniform temperature. This may lead to differential shrinkage during cooling and produce warping, locked-up internal stresses, and weakening of the part.

Warping may be prevented by a suitable mounting. Internal stresses in plastics that are more subject to creep and cold flow tend to relieve themselves slowly; warming the part accelerates the process. Internal stresses in polystyrene and other brittle plastics can be removed by an annealing process similar to the one used in glass manufacture. It involves a controlled heating-cooling cycle, and for plastics it is obtained by immersing the parts in a liquid held at the proper temperature, followed by very slow cooling. Polystyrene for example can be heated in water at 80°C and then slowly cooled to 65°C. It is then cooled in undisturbed air.

The relatively high thermal expansion of plastics poses a problem in the use of molded metal inserts which are sometimes required for electrical contacts, screw thread mountings, or increased strength. To minimize stresses due to inserts, manufacturers usually use plastics with low coefficient of expansion.

Phenolics and ureas are commonly used because their coefficient of expansion are among the lowest of the common plastics.

For many plastics the use of molded metal inserts is not satisfactory because of the excessive stress produced. As an example, polystyrene with brass inserts on cooling from the molding temperature of 160 to 20°C produces a strain of $(70 - 17) \times 10^{-6} \times (160 - 20)$ or 0.0074. For an elastic modulus of 0.46×10^6 psi (3.2 GPa), the internal stresses become 3,400 psi (23 Mpa). The presence of this much internal stress renders the part useless, since the tensile strength of polystyrene is only 3,600 psi (25 Mpa).

However, by use of an appropriate filler the thermal expansion of plastics and, hence, the internal stresses can be reduced. Addition of 11%

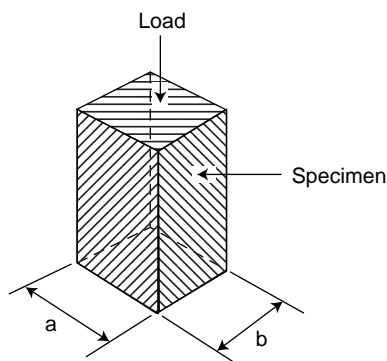


FIGURE 3.70 Test for compressive strength of plastics. Compressive strength (lbf/in.² or kgf/cm²) = load (lbf or kgf)/ $a \cdot b$ (in.² or cm²). Standard test methods: ASTM D795, BS 2782 method 303, ISO R604.

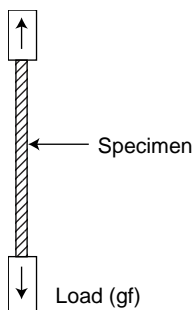


FIGURE 3.71 Test for tenacity of filaments, cords, twines, etc. Tenacity (gf/denier) = breaking load (gf)/denier of specimen. (Denier of filaments, cords, twines, etc., is equal to the weight in grams of 9,000 meters of the sample.)

sion of plastics is used to advantage. One example is the shrink fitting of handles of cellulose nitrate on screwdrivers. Another example is in mold design where the shrinkage on cooling is sufficient to permit a small undercut.

3.6.3 Thermal Conductivity

Thermal conductivities of plastics are relatively low and approximate $0.0004 \text{ (cal-cm)} / (\text{°C-cm}^2\text{-sec})$. The corresponding values are 0.95 for copper, 0.12 for cast iron, 0.002 for asbestos, 0.0008 for wood, and 0.0001 for cork (SI values in J/s-m-k are obtained by multiplying by 418.7). Because of their low thermal conductivities, plastics are used for handles to cooking utensils and for automobile steering wheels. The low thermal conductivity is also responsible for the pleasant feel of plastic parts. Quite hot or quite cold objects can be handled with less difficulty if they are made of plastic, since the thermal insulation afforded by the plastic prevents a continuous rush of heat energy to (or from) the hand.

Both thermal conductivity and temperature resistance of plastics have to be considered for their use at high temperatures. As an example consider a teapot handle; it must not deform even at 100°C . Therefore,

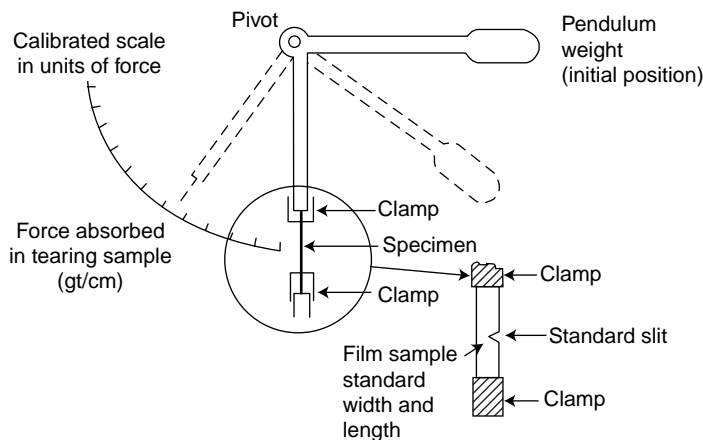


FIGURE 3.72 Test for tear propagation resistance of plastic film and thin sheeting. Tear resistance (gf/cm/mil) = force required to tear sample (gf/cm)/thickness of film (mil). Standard test methods: ASTM D1922, BS 2782 method 308B.

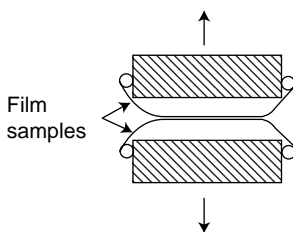


FIGURE 3.73 Tests for blocking of plastic film. Blocking force (lbf/in.² or kgf/cm²) = load (lbf or kgf)/initial area of films in contact (in.² or cm²). Standard test method: ASTM D1893.

common thermoplastics such as cellulose acetate are ruled out, but both a wood-flour-filled and an asbestos-filled phenolic might be considered.

The thermal conductivity of a mixture is nearly proportional to the volume percentage of each component. Wood-flour-filled phenolic has a higher thermal conductivity than the pure resin, but the conductivity of this composite is still low enough to justify its use as the handle to a teapot. This composite can also withstand temperatures up to 100°C sufficiently well to give the handle a reasonable service life. For parts subjected to higher temperatures, asbestos-filled phenolic is a

better choice. It can be used as the insulating connection to an electric iron, for example.

Design of a handle determines to a great extent its service life. Quite often handles are found fastened directly to the hot object without regard for any temperature limitation; at the junction the plastic becomes brittle because of high temperature, and failure occurs. If the handle can be separated from the heated part and some cooling arrangement is included as part of the design, improved performance is to be expected.

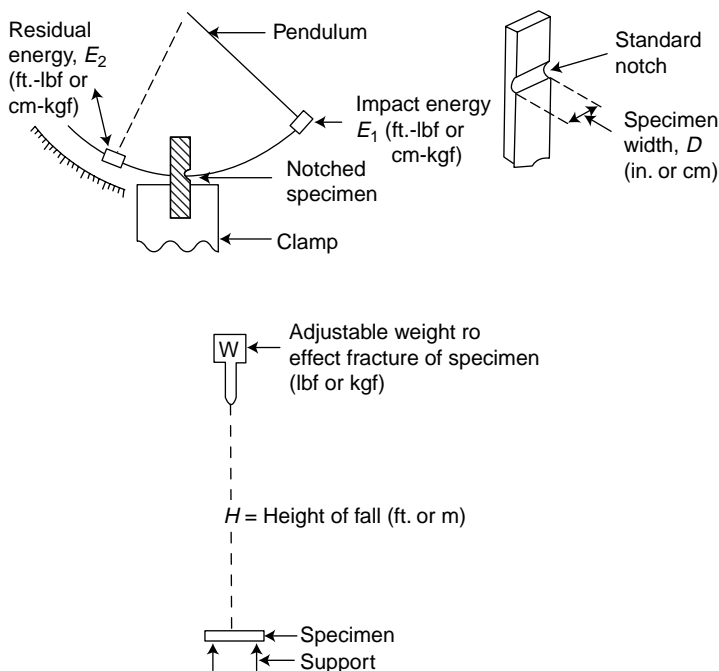


FIGURE 3.74 Tests for impact resistance of plastics. Izod impact strength = $(E_1 - E_2)/D$ ft-lbf/in. of notch or cm-kgf/cm of notch. Standard test methods: ASTM D256; BS 2782 method 306A, ISO R180. Falling weight impact strength = $W \cdot H$ ft-lbf or m-kgf. (F_{50} is the energy required to fracture 50% of the specimens.) Standard test method: BS 2782 method 306 B.

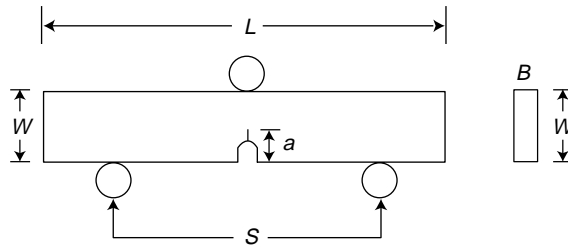


FIGURE 3.75 Test for fracture toughness of plastics. Specimen in three-point bending configuration, as shown, is loaded in a testing machine that has provision for autographic recording of load applied to the specimen. Specimen dimensions: L , length (mm); W , width (mm); B , thickness (mm); S , span length (mm); a , initial crack length (mm). Plane strain fracture toughness, $K_{Ic} = PSf(a/W)/BW^{3/2}$, where P = load (N) determined from load displacement record; $f(a/W)$ = geometric factor. Example: $L = 64$ mm, $W = 10$ mm, $B = 3$ mm, $S = 40$ mm, $a = 3.2$ mm, $P = 50.88$ N, $f(a/W) = 1.61$ (from ASTM standard), $K_{Ic} = 34.3$ N mm $^{-3/2} = 1.09$ MPa m $^{1/2}$. Standard test method: ASTM E399-74.

3.6.4 Transition Temperatures and Temperature Limitations

Both first- and second-order transitions are observed in polymers. Melting and allotropic transformations are accompanied by latent-heat effects and are known as first-order transitions. During second-order transitions, changes in properties occur without any latent-heat effects. Below the second-order-transition temperature (glass transition temperature) a rubberlike material acts like a true solid (see [Chapter 1](#)). Above this temperature the fixed molecular structure is broken down partially by a combination of thermal expansion and thermal agitation. The glass transition temperature of polystyrene is 100°C; below 100°C polystyrene is hard and brittle, and above 100°C it is rubberlike and becomes easily deformed.

The design engineer often requires to know the maximum temperature for which a polymer can be used in a given application. This depends largely on two independent factors: (1) the thermal stability of the polymer, particularly in air; and (2) the softening behavior of the polymer.

Thermal stability testing requires the study of the change in properties on aging at various service temperatures. The relationship between structure and stability was considered briefly in [Chapter 1](#) and will be considered again in [Chapter 5](#). The use of additives for improving such stability is discussed in [Chapter 1](#).

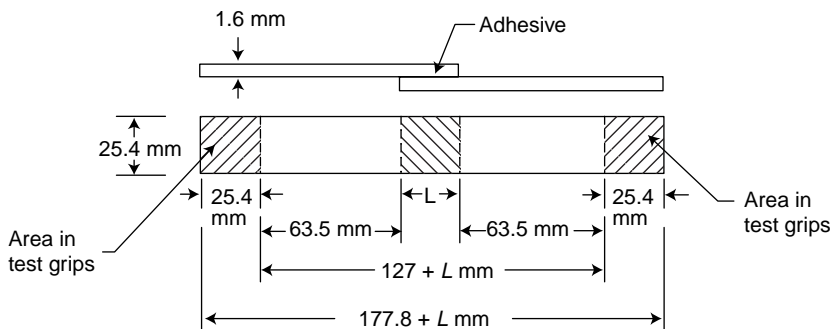


FIGURE 3.76 Form and dimensions of test specimen for single-lap-joint shear test to determine shear strengths of adhesives for bonding metals (standard test method: ASTM D1002-94). Recommended length of overlap (L) for most metals of 1.62 mm in thickness is 12.7 mm. Specimen is placed in grips of a testing machine so that outer 25.4 mm (1 in.) of each end is in contact with the jaws. Load is applied at the rate of 80–100 kg/cm 2 (1,200–1,400 psi) of shear area per min and continued till failure occurs.

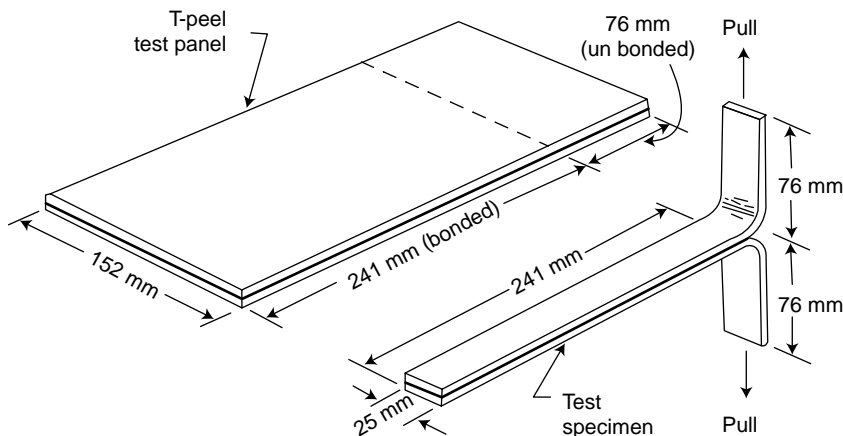


FIGURE 3.77 Test panel and T-type test (T-peel test) specimen for peel resistance of adhesives (standard test method: ASTM D1876-95). The bent, unbonded ends of test specimen are clamped in test grips of tensile testing machine and load applied at a constant head speed of 254 mm (10 in.). Average peeling load (in pounds per inch of specimen width) is determined for the first 127 mm (5 in.) of peeling after the initial peak.

The rigidity of a polymer is determined by the ease with which polymer molecules are deformed under load. Young's modulus is a fundamental measure of the rigidity or stiffness of a material. It is thus clear from [Figure 1.13](#) that the softening point is associated with the T_g for amorphous polymers and with the T_m for highly crystalline polymers. In addition, there are many polymers that soften progressively between T_g and T_m and the value determined for the softening point can depend significantly on the test method used.

Two particular test methods have become very widely used. These are the Vicat softening point test and the test widely known as the heat distortion temperature test (also called the deflection temperature under load test). In the Vicat softening point test a sample of polymer is heated at a specified rate temperature increase and the temperature is noted at which a needle of specified dimensions indents into the polymer a specified distance under a specified load.

The heat-distortion temperature is defined as the temperature at which the midpoint of a beam 1/2 by 1/2 by 5 in. supported 1/2-in. from each end, shows a net deflection of 0.01 in. when loaded centrally with 2.5 kg and heated at the specified rate of 2°C/min. Testing is also done at one-quarter of this load. For most materials the two heat-distortion temperatures are within 10°.

A large difference in these two heat distortion temperature indicates a material sensitive to temperature change, and for such materials at any elevated temperature stress should be minimum up to the heat-distortion temperature. A plastic is expected to maintain its shape under load, and hence this temperature represents an upper limiting point at which a plastic may be used.

Recommendations of upper temperature limits for plastics are usually based on general experience, although some consideration is given to high-load and low-load heat-distortion temperatures. The size and shape of the part as well as its molding

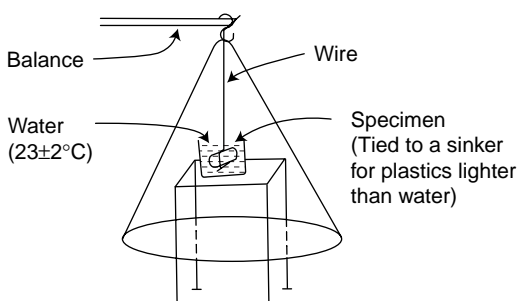


FIGURE 3.78 Test for specific gravity and density of plastics. $\text{Sp. gr.} = a/(a - w - b)$ where $a = \text{wt. of specimen without wire}$, $b = \text{wt. of specimen completely immersed}$ and of the wire partially immersed in water, and $w = \text{wt. of partially immersed wire}$. Standard test method: ASTM D792.

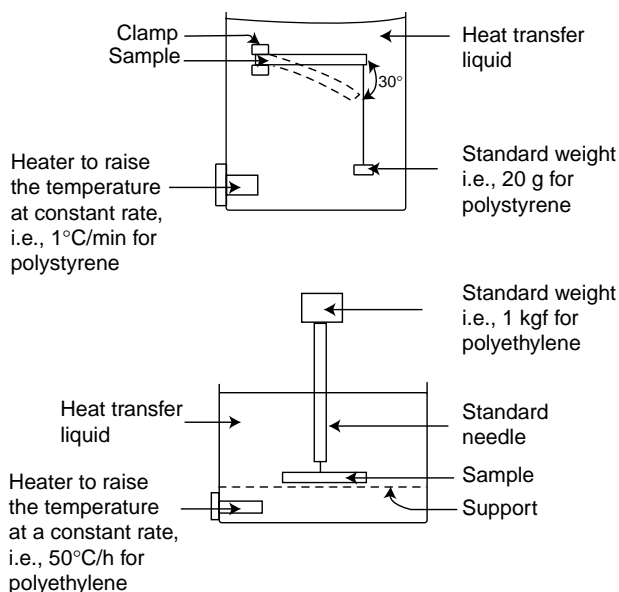


FIGURE 3.79 Tests for softening temperatures of plastics. Cantilever softening point is the temperature at which the sample bends through 30°. Standard test method: BS 2782 method 102 C. Vicat softening point is the temperature at which the needle penetrates 1 mm into the sample. Standard test methods: ASTM D1525, BS 2782 method 102D, ISO R306.

conditions govern to a certain extent the maximum permissible temperature; service conditions such as temperature variations and humidity are also important.

3.6.5 Standard Properties of Plastics

Figure 3.67 through Figure 3.93 illustrate schematically (in simplified form) the bases of some of the standard properties of plastics [33]. Where standard test methods have been developed, these have been included. The principles of the different tests are shown, and the properties measured are indicated.

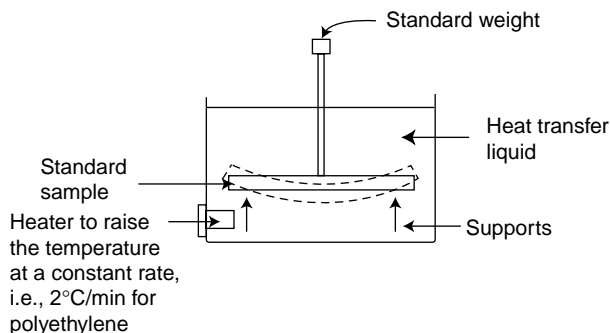


FIGURE 3.80 Test for deflection temperature of plastics under flexural load. Heat distortion temperature is the temperature at which a sample deflects by 0.1 in. (2.5 mm). Two measurements are made and quoted: (a) with a stress of 66 lbf/in.² (4.6 kgf/cm²) and (b) with a stress of 264 lbf/in.² (18.5 kgf/cm²). Standard test methods: ASTM D648, BS 2782 method 102, ISO R75.

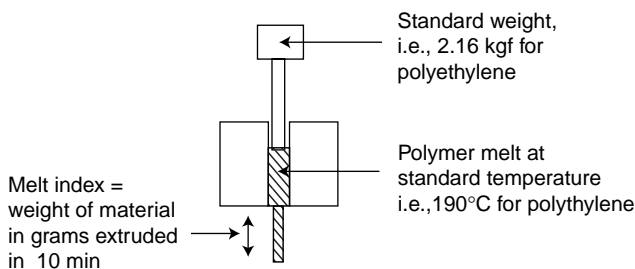


FIGURE 3.81 Melt index of plastics. The test measures the rate of flow of polymer melt. It provides an indication of the ease of processing. Standard test methods: ASTM D 1238, BS 2782 method 105C, ISO R292.

Note that the property values of plastics are highly dependent on the specimen preparation, equipment, and testing techniques used. For this reason it is essential to refer to the appropriate official standard test method when executing the work.

3.7 Identification of Common Plastics

The first step in the identification of polymers is a critical visual examination. While the appearance of the sample may indicate whether it is essentially a raw polymer or a compounded and processed item, learning about its form, feel, odor, color, transparency or opacity, softness, stiffness, brittleness, bounce, and surface texture may be important in the process of the identification of the polymer. For example, polystyrene, the general purpose polymer, is transparent and brittle, and produces a characteristic metallic tinkle when objects molded from it are dropped or struck.

Identification of plastics [34] is carried out by a systematic procedure: preliminary test, detection of elements, determination of characteristic values, and, finally, specific tests. For an exact identification, however, the test sample should first be purified so that it contains no additives (plasticizers, fillers, pigments, etc.) that may affect the results of an analysis. Purification is achieved by solvent extraction; either the material is dissolved out and polymer is obtained by reprecipitation or evaporation of the solvent, or the pure polymer remains as the insoluble residue. The solvent varies, and a general method cannot be given. However, for many materials particularly for those in which additives do not interfere, the unpurified material can be investigated and qualitative preliminary tests used.

In general, the following series of investigations should be carried out for preliminary tests of the material: (1) behavior on heating in an ignition tube and in the flame; (2) qualitative detection of heteroelements such as N, S, and halogens; (3) determination of properties such as density, refractive index, and melting point or range; (4) determination of solubility as an aid to polymer identification; and (5) ash or sulfated ash determination as a test for inorganic additives (fillers, pigments, stabilizers).

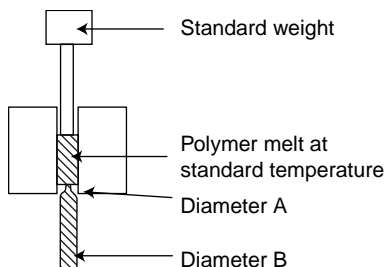


FIGURE 3.82 Measurement of swelling of die extrudate. Die swell ratio = B/A .

3.7.1 Behaviors on Heating and Ignition

Many polymers can be roughly identified by their behavior when carefully heated and ignited. Nitrocellulose and plastics containing this (e.g., celluloid) burn with explosive violence and other materials such as poly(vinyl chloride) or fluoro-hydrocarbons decompose with the evolution of poisonous or irritating vapors. Only

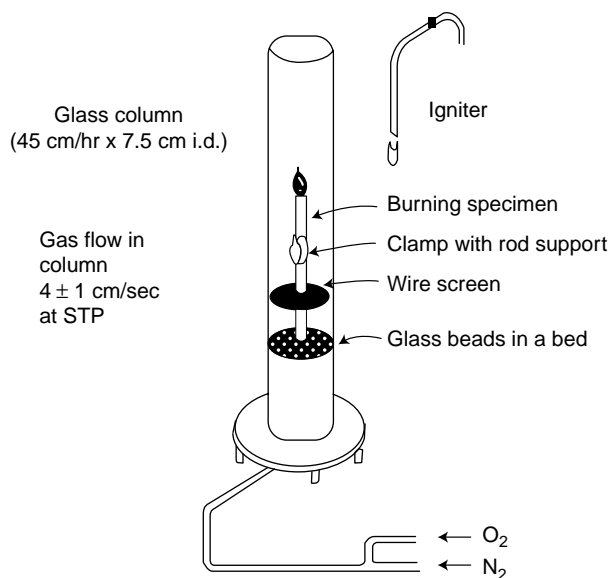


FIGURE 3.83 Determination of oxygen index. Oxygen index, $n\% = 100 \times O_2 / (O_2 + N_2)$, where O_2 , volumetric flow rate of oxygen, cm^3/sec , at the minimum concentration necessary to support flaming combustion of a material initially at room temperature and N_2 , corresponding flow rate of nitrogen, cm^3/sec . Standard test method: ASTM D2863.

small quantities of material should therefore be taken for heating tests. The heating should be done gently, because if the heating is too rapid or intense, the characteristic changes may not be observed.

In a typical procedure, a small piece or amount (0.1 g) of the test sample is placed on a cleaned glass or stainless steel spatula, previously heated to remove any traces of combustible or volatile materials, and then warmed gently over a small colorless Bunsen flame until the sample begins to fume. The decomposing sample is removed from the flame and the nature of the fume or gas is examined with respect to color, odor, inflammability, and chemical identity including acidity, alkalinity, etc.

The sample is next moved to the hottest zone of the small Bunsen flame and note is taken of the

following: (1) if the material burns and if so, how readily; (2) the nature and color of the flame as the material burns; (3) whether the material is self-extinguishing or continues to burn after removal from the flame, and (4) the nature of the residue.

Observations on heating and ignition of some common polymers are listed in [Table 3.8](#).

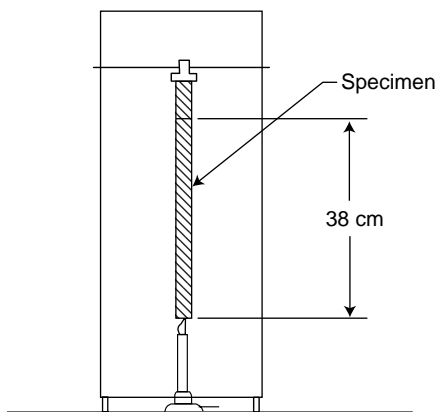


FIGURE 3.84 Test for rate of burning. Burning rate = $38 \text{ (cm)}/t \text{ (min)}$. Standard test method: ASTM D568.

3.7.2 Tests for Characteristic Elements

The results of tests for characteristic elements such as nitrogen, sulfur and halogens may serve to roughly indicate the nature of the unknown material, including the nature of the base polymer and additives, if present. The following tests may be performed for qualitative detection of N, S, and halogens.

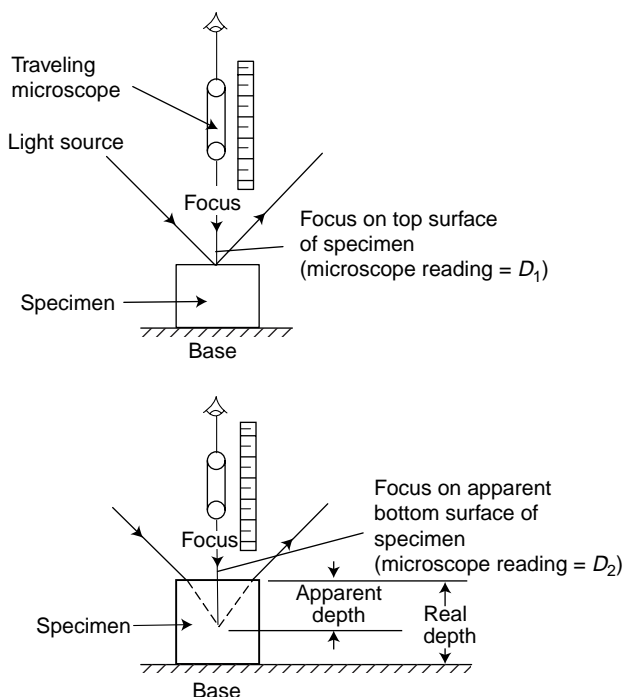


FIGURE 3.85 Test for index of refraction of transparent plastics. Refractive index = real depth (measured with vernier)/apparent depth ($D_2 - D_1$). Standard test method: ASTM D542, ISO R489.

1. **Nitrogen.** Above 50 mg of the test material is heated carefully in an ignition tube with twice the amount of freshly cut sodium, until the sodium melts. A further small amount of material is added and the tube is heated to red heat. It is then dropped carefully into water (20 ml) in a mortar. The solid is powdered and the solution filtered.

A little freshly prepared ferrous sulfate is added to the filtrate and the latter boiled for 1 min. It is acidified with dilute hydrochloric acid, and 1–2 drops of ferric chloride solution added. A deep blue coloration or precipitate (Prussian blue) indicates nitrogen (if very little nitrogen is present, a green–blue color is formed initially). This test sometimes fails with substances containing nitro-groups and with nitrogen-containing heterocyclic compounds.

2. **Sulfur.** The fusion is carried out as for nitrogen. The filtrate (2 ml) is acidified with acetic acid and a few drops of an aqueous solution of lead acetate is added. A black precipitate of lead sulfide indicates the presence of sulfur.
3. **Halogens.** The fusion is carried out as for nitrogen. The filtrate (2 ml) is acidified with dilute nitric acid, boiled in the fume cupboard to remove H_2S and HCN , and then a few drops of silver nitrate solution is added. A white precipitate, turning grey–blue, indicates chlorine, a yellowish precipitate indicates bromine and a yellow precipitate indicates iodine.

In Beilstein's test, which provides a simple means of detecting halogens, a minute quantity of the test material is placed on a copper wire (initially heated in a nonluminous bunsen flame until the flame appears colorless and then cooled) and heated in the outer part of the flame. Carbon burns first with a luminous flame. A subsequent green to blue–green color, produced by volatilized copper halide, indicates halogen (chlorine, bromine, iodine).

The different polymers may be classified into several groups according to the element present as shown in Table 3.9. The focus of identification may be further narrowed down on the basis of other preliminary observations, e.g., fusibility or otherwise, melting point or range, heat distortion temperature, flame tests

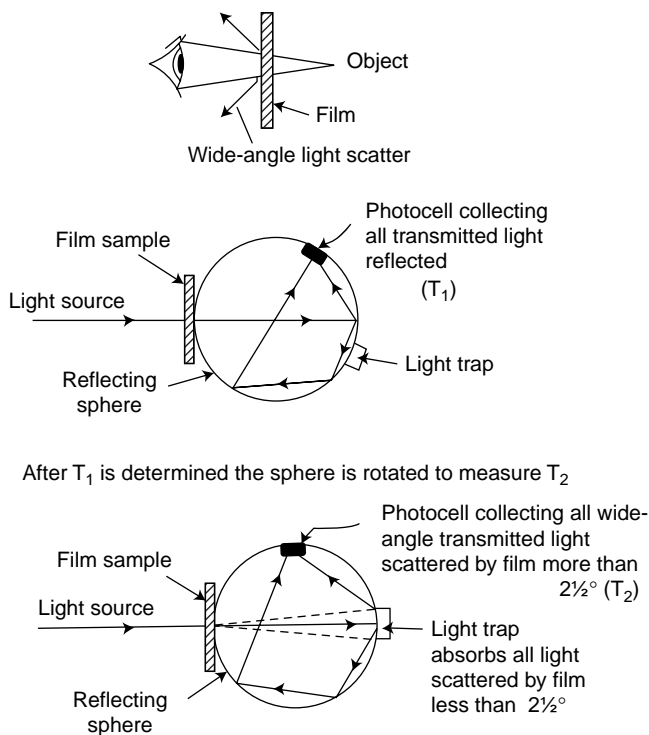


FIGURE 3.86 Test for haze of transparent plastics. Haze, % = $100 \times T_2/T_1$. A low haze value is important for good short distance vision. Standard test method: ASTM D1003.

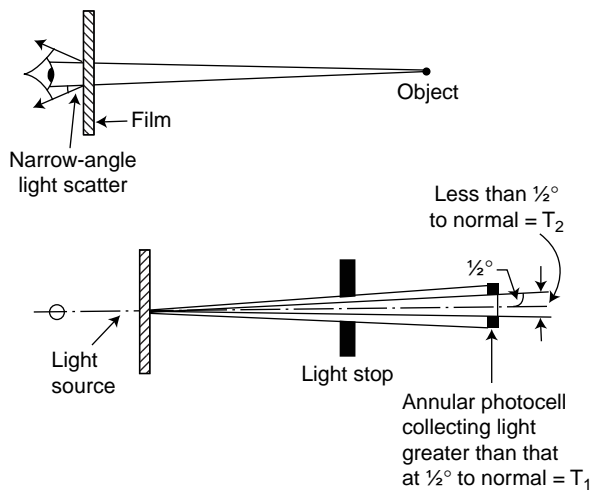


FIGURE 3.87 Measurement of narrow-angle light-scattering property of plastic film. Clarity, % = $100 \times T_1/(T_1 + T_2)$.

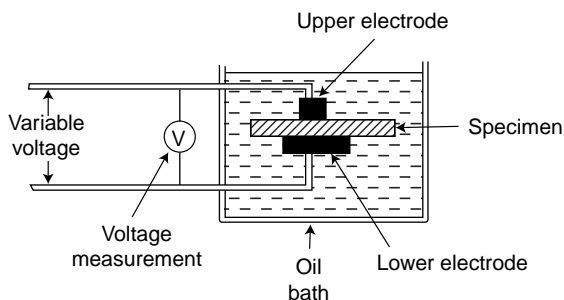


FIGURE 3.88 Test for dielectric strength of solid insulating materials. Dielectric strength (V/mil) = maximum voltage before failure (V)/thickness of specimen (mil). Standard test methods: ASTM D149, BS 2782 method 201.

and tests for thermal degradation, and solubility or extractability in water or different organic solvents. The solubility behaviors of common polymers are compared in [Table 3.10](#).

3.7.3 Specific Tests

When the observations and results of preliminary tests have been considered and most of the possible structures for the polymer base eliminated, an exact identification can be made by carrying out specific tests [35]. Some specific tests for ready identification of specific polymers are described below.

1. *Tests for polystyrene and styrenic copolymers.* The test depends on the aromatic rings of the styrene units in the polymer chain. The polymer sample (0.1 g) is heated under reflux in concentrated nitric acid and the clear mixture is poured into water (25 ml) to yield a pale yellow precipitate which is then extracted with ether (2×25 ml). The ether extracts are combined and washed thoroughly with water (2×5 ml), then extracted with dilute sodium hydroxide solution (2×5 ml) and finally with water (5 ml).

The alkaline extracts and the aqueous extract are combined and the nitro compounds present in the mixture are reduced by adding granulated zinc (1 g) and concentrated hydrochloric acid and warming gently. The solution is cooled, filtered and then diazotized with a dilute solution

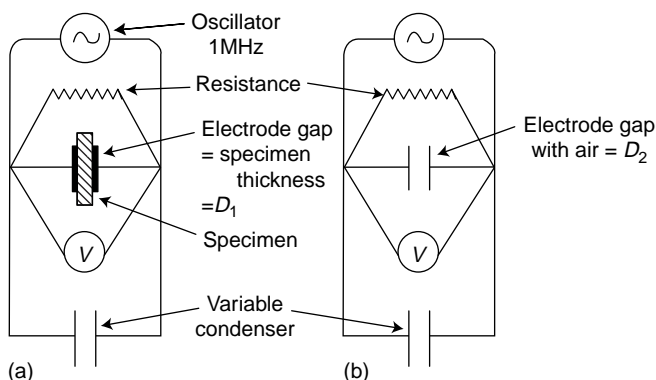


FIGURE 3.89 Test for permittivity (dielectric constant) of insulating materials. (a) Position of maximum voltage obtained with sample by adjusting variable capacitor. Electrode gap = specimen thickness = D_1 ; (b) position of maximum voltage obtained with air by adjusting electrode gap to D_2 [variable capacitor remains as set in (a)]. Dielectric constant = D_1 (in. or mm)/ D_2 (in. or mm). Standard test methods: ASTM D150, BS 2782 method 207A.

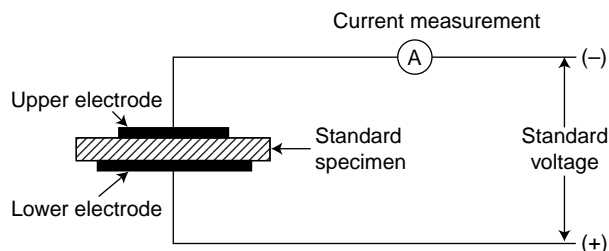


FIGURE 3.90 Test for DC resistance of insulating materials. Electrical resistance of specimen (ohm)=applied voltage (V)/current measured (A). Volume resistivity (ohm-cm)=resistance of specimen (ohm) \times area of upper electrode (cm²)/specimen thickness (cm). Standard test methods: ASTM D257, BS 2782 method 202.

(5 ml) of sodium nitrite under ice-cooled condition. The solution is finally poured into excess of alkaline β -naphthol solution producing a deep red color.

2. *Test for poly(vinyl chloride).* Specific tests for chlorine containing polymers are performed only when the presence of chlorine is confirmed by preliminary test. The simplest method of chlorine determination is the Beilstein test, described previously. Plasticizers are removed from the test material by ether extraction and the Beilstein test for chlorine is repeated to make certain that chlorine is still present. The material is then dissolved in tetrahydrofuran, filtered and the polymeric product reprecipitated by adding methanol.

On addition of a few drops of a $\sim 10\%$ methanolic solution of sodium hydroxide to 2–5 ml of $\sim 5\%$ solution of the plasticizer free material, the mixture changes with time from colorless to light yellow–brown, dark brown, and finally to black.

In another test, poly(vinyl chloride) and vinyl chloride polymers readily form brown coloration and eventually dark brown precipitates when their pyridine solutions are boiled and treated with a few drops of methanolic sodium hydroxide (5%).

3. *Test for poly(vinylidene chloride).* Poly(vinylidene chloride), when immersed in morpholine, develops a brown color both in the liquid and the partially swollen polymer. The change takes place faster if the mixture is warmed in a water bath.
4. *Test for poly(vinyl alcohol) and poly(vinyl acetate).* When a small volume of iodine solution (0.2 g iodine and 1.0 g KI dissolved in 20 ml of a 1:1 alcohol–water mixture and diluted to 100 ml using 2N hydrochloric acid solution) is added to an equal volume of 0.25% neutral or acidic solution of

poly(vinyl alcohol), a blue color develops almost immediately or on addition of a pinch of borax into the solution. Poly(vinyl acetate), however, turns deep brown on contact with the dilute iodine solution.

5. *Test for polyacrylonitrile and acrylonitrile copolymers.* When a strip of cupric acetate paper that is freshly moistened with a dilute solution of benzidine in dilute acetic acid is held in the pyrolytic vapors of polyacrylonitrile or its copolymers, a bright blue color develops readily. In another test, if the condensed pyrolyzate of polyacrylonitrile or its copolymers is made alkaline, boiled with a trace of ferrous sulfate, and then acidified, Prussian blue precipitate is readily produced.

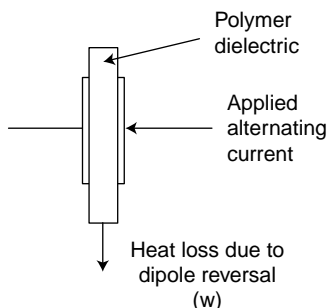


FIGURE 3.91 Test for AC loss characteristics of solid insulating materials. Power factor = $W/V \times I$, where W = power loss in watts and $V \times I$ = effective sinusoidal voltage \times current in volt-amperes. Standard test methods: ASTM D150, BS 2782 method 207A.

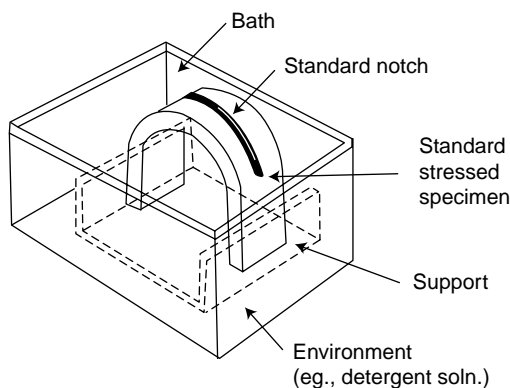


FIGURE 3.92 Test for environmental stress cracking of ethylene plastics. Stress cracking resistance (F_{50}) = time taken for 50% of the specimens to fail (h). Standard test method: ASTM D1693.

examples are phenol-, urea-, and melamine-formaldehyde resins, polyoxymethylene and poly(vinyl formal). Formaldehyde is evolved when these are thermally treated or boiled with water in the presence of an acid (H_2SO_4).

The aqueous extracts or acid distillates are treated with chromotropic acid (1,8-dihydroxynaphthalene-3, 6-disulfonic acid). A few drops of 5% aqueous chromotropic acid solution are added to the aqueous test solution and then an excess of concentrated sulfuric acid is added, and the mixture preferably warmed to nearly $100^\circ C$ for a few minutes. In the presence of formaldehyde, the solution turns violet/dark violet.

Phenol, urea, and melamine are also obtained as intermediates on acid hydrolysis of the corresponding formaldehyde condensate resins and appropriate tests for phenol, urea, and melamine may be employed for identification purposes.

6. *Test for phenolic resins.* The test material (dry) is heated in an ignition tube over a small flame. The mouth of the tube is covered with a filter paper, prepared by soaking it in an ethereal solution of 2,6-dibromoquinone-4-chloro-imide and then drying it in air. After the material has been pyrolyzed for about a minute, the paper is removed and moistened with 1–2 drops of dilute ammonia solution. A blue color indicates phenols (care must be taken with plastics that contain substances yielding phenols on pyrolysis, e.g., phenyl and cresyl phosphate, cross-linked epoxide resins, etc.).

7. *Test for formaldehyde condensate resins.* Formaldehyde enters into the composition of several resins and polymers. Common

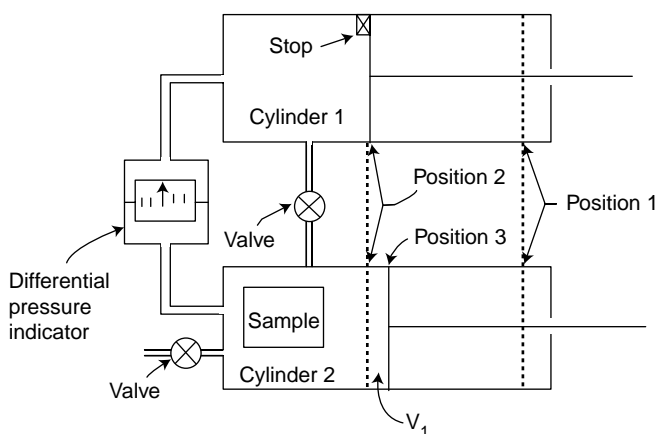


FIGURE 3.93 Determination of open cell content of rigid cellular plastics. Open cell content (approx.) = $100 (V - V_1)/V$, where V , displacement volume of specimen, cm^3 and V_1 , geometric volume of specimen, cm^3 . Standard test method: ASTM D2856.

TABLE 3.8 Heating Tests of Some Common Polymers

Polymer	Color of Flame	Odor of Vapor	Other Notable Points
<i>The material burns but self-extinguishes on removal from flame</i>			
Poly(vinyl chloride)	Yellow–orange, green bordered	Resembles hydrochloric acid and plasticizer (usually ester like)	Strongly acidic fumes (HCl), black residue
Poly(vinylidene chloride)	As above	Resembles hydrochloric acid	As above
Polychloroprene	Yellow, smoky	As above	As above
Phenol-formaldehyde resin	Yellow, smoky	Phenol, formaldehyde	Very difficult to ignite, vapor reaction neutral
Melamine-formaldehyde resin	Pale yellow, light	Ammonia, amines (typically fish like), formaldehyde	Very difficult to ignite, vapor reaction alkaline
Urea-formaldehyde resin	As above	As above	As above
Nylons	Yellow–orange, blue edge	Resembling burnt hair	Melts sharply to clear, flowing liquid; melt can be drawn into a fiber; vapor reaction alkaline
Polycarbonate	Luminous, sooty	Phenolic	Melts and chars
Chlorinated rubber	Yellow, green bordered	Acrid	Strongly acidic fumes, liberation of HCl; swollen, black residue
<i>The material burns and continues burning on removal from flame</i>			
Polybutadiene (BR)	Yellow, blue base, smoky	Disagreeable, sweet	Chars readily; vapor reaction neutral
Polyisoprene (NR, gutta percha, synthetic)	Yellow, sooty	Pungent, disagreeable, like burnt rubber	As above
Styrene-butadiene rubber (SBR)	Yellow, sooty	Pungent, fruity smell of styrene	As above
Nitrile rubber (NBR)	Yellow, sooty	Like burnt rubber/burnt hair	As above
Butyl rubber (IIR)	Practically smoke free candle like	Slightly like burnt paper	Melt does not char readily
Polysulfide rubber (polymer itself emits unpleasant, mercaptan like odor)	Smoke-free, bluish	Pungent; smell of H ₂ S	Yellow, acidic (SO ₂) fumes
Cellulose (cotton, cellophane, viscose rayon, etc.)	Yellow	Burnt paper	Chars, burns without melting
Cellulose acetate	Yellow–green, sparks	Acetic acid, burnt paper	Melts, drips, burns rapidly, chars, acidic fumes
Cellulose acetate butyrate	Dark yellow (edges slightly blue), somewhat sooty, sparks	Acetic acid/butyric acid, burnt paper	Melts and forms drops which continue burning
Cellulose nitrate (plasticized with camphor)	Yellow	Camphor	Burns very fast, often with explosion
Methyl cellulose	Yellow, luminous	Burnt paper	Melts and chars
Ethyl cellulose	Pale yellow with blue–green base	Slightly sweet, burnt paper	Melts and chars
Polyacrylonitrile	Yellow	Resembling burnt hair	Dark residue; vapor reaction alkaline
Poly(vinyl acetate)	Yellow, luminous, sooty	Acetic acid	Sticky residue, acidic vapor
Poly(vinyl alcohol)	Luminous, limited smoky	Unpleasant, charry smell	Burns in flame, self extinguishing slowly on removal; black residue

(continued)

TABLE 3.8 (Continued)

Polymer	Color of Flame	Odor of Vapor	Other Notable Points
Poly(vinyl butyral)	Bluish (yellow edge)	Like rancid butter	Melts, forms drops
Poly (vinyl acetal)	Purple edge	Acetic acid	Does not drip like poly (vinyl butyral)
Poly(vinyl formal)	Yellow–white	Slightly sweet	Does not drip like poly(vinyl butyral)
Polyethylene	Luminous (blue center)	Like paraffin wax (extinguished candles)	Melts, forms drops; droplets continue burning
Poly(α -olefins)(PP, EPR, etc.)	As above	As above	As above
Polystyrene	Luminous, very sooty	Sweet (styrene)	Softens, easily ignited
Poly(methyl methacrylate)	Luminous, yellow (blue, edge), slightly sooty, crackling	Sweet, fruity	Softens, chars slightly

Source: From Krause, A. and Lange, A. 1969. *Introduction to Chemical Analysis of Plastics*. Iliffe Books Ltd, London; Ghosh, P. 1990. *Polymer Science and Technology of Plastics and Rubber*. Tata McGraw-Hill, New Delhi, India.

- a. *Phenol*. On addition to the extract (10 ml), approximately 0.5N potassium hydroxide (8–10 ml) and 2 ml of diazotized *p*-nitroaniline (5% sodium nitrite solution added to an ice-cold solution of 2–5 mg of *p*-nitroaniline dissolved in 500 ml of approximately 3% hydrochloric acid, until the solution becomes just colorless), a red or violet color develops indicating phenol. No differentiation between phenol and its homologs is possible by this test.
- b. *Urea and melamine*. The aqueous extract is divided into two parts. (solutions 1 and 2). Solution 1 is made alkaline with dilute sodium hydroxide, and 1 ml of sodium hypochlorite solution is added. Solution 2 is treated with freshly prepared furfural reagent (5 drops of pure, freshly distilled furfural, 2 ml of acetone, 1 ml of concentrated hydrochloric acid, and 2 ml of water).

TABLE 3.9 Classification of Most Common Polymers According to Elements Present

Group	Element Found	Rubbers ^a	Plastics/Fibers
Group 1	N	Nitrile (NBR), polyurethane (ester/ether urethanes)	Cellulose nitrate, silk, polyamides, polyimides, polyurethanes, polyacrylonitrile, SAN and ABS resins, urea-formaldehyde resins, melamine-formaldehyde resins, etc.
Group 2	S	S-vulcanized diene rubbers (NR, IR, SBR, BR, CR, IIR, EPDM, NBR), polysulfide rubbers and chlorosulfonated polyethylenes.	Wool, polysulfones, ebonite, etc.
Group 3	Cl	Polychloroprene, chlorosulfonated polyethylenes, etc.	Poly(vinyl chloride), poly(vinylidene chloride) and related copolymers, polychlorotrifluoroethylene, chlorinated or hydrochlorinated rubber, etc.
Group 4	Absence of N, S, Cl, etc.	Peroxide cross-linked or unvulcanized hydrocarbon rubbers (NR, IR, SBR, BR, IIR, EPDM, EPR, etc.)	Petroleum resins, coumaroneindene resins, cellulose and cellulose derivatives other than cellulose nitrate, polyesters, polyethers or acetal resins, polyolefins, polystyrene, poly(methyl methacrylate), poly(vinyl acetate/alcohol), etc.

^a See [Appendix A3](#) for abbreviations.

TABLE 3.10 Solubility Behavior of Some Common Plastics

Resin	Soluble In	Insoluble In
Polyolefins		
Polyethylene	Dichloroethylene, xylene, tetralin, decalin (boiling)	Alcohols, esters, halogenated hydrocarbons
Polypropylene	Chloroform, trichloroethylene, xylene, tetralin, decalin (boiling)	Alcohols, esters
Polyisobutylene	Ethers, petroleum ether	Alcohols, esters
Poly(vinyl chloride)	Dimethyl formamide, tetrahydrofuran, cyclohexanone	Alcohols, hydrocarbons, butyl acetate
Poly(vinylidene chloride)	Butyl acetate, dioxane, ketones, tetrahydrofuran	Alcohols, hydrocarbons
Polytetrafluoroethylene	Insoluble	All solvents
Polychlorotrifluoroethylene	<i>o</i> -Chlorobenzotrifluoride (above 120°C)	All solvents
Polystyrene	Benzene, methylene chloride, ethyl acetate	Alcohols, water
ABS	Chlorinated hydrocarbons, eg., <i>p</i> -dichlorobenzene	Alcohols, water
Polybutadiene	Benzene	Aliphatic hydrocarbons, alcohols, esters, ketones
Polyisoprene	Benzene	Alcohols, esters, ketones
Acrylics		
Polyacrylonitrile	Dimethylformamide and nitrophenol	Alcohols, esters, ketones, hydrocarbons
Polyacrylamide	Water	Alcohols, esters, hydrocarbons
Esters of polyacrylic acid	Aromatic hydrocarbons, esters, chlorinated hydrocarbons, ketones, tetrahydrofuran	Aliphatic hydrocarbons
Esters of polymethacrylic acid	Aromatic hydrocarbons, chlorinated hydrocarbons, esters, ketones, dioxane	Aliphatic hydrocarbons alcohols, ethers
Poly(vinyl acetate)	Aromatic hydrocarbons, chlorinated hydrocarbons, ketones, methanol	Aliphatic hydrocarbons
Poly(vinyl alcohol)	Formamide, water	Aliphatic and aromatic hydrocarbons, alcohols, ethers, esters, ketones
Poly(vinyl acetals)	Esters, ketones, tetrahydrofuran, (butyrals in 9:1 chloroform- methanol mixture)	Aliphatic hydrocarbons, methanol
Poly(vinyl ethers)		
Methyl ether	Water, alcohol, benzene, chlorinated hydrocarbons, ethers, esters	Petroleum ether
Ethyl ether	Petroleum ether, benzene, chlorinated hydrocarbons, alcohols, ethers, esters, ketones	Water
Polyesters	Benzyl alcohol, nitrated hydrocarbons, phenols	Alcohols, esters, hydrocarbons
Polycarbonate	Chlorinated hydrocarbons, cyclohexanone, dimethyl formamide, cresol	(Only swelling in usual solvents)
Nylon	Formic acid, phenols, trifluoroethanol	Alcohols, esters, hydrocarbons
Molded phenolic resins	Benzylamine (at 200°C)	All common solvents
Molded amino resins (urea, melamine)	Benzylamine (at 160°C)	All common solvents

(continued)

TABLE 3.10 (Continued)

Resin	Soluble In	Insoluble In
Polyurethanes		
Noncross-linked	Methylene chloride, hot phenol, dimethylformamide	Petroleum ether, benzene, alcohols, ethers
Cross-linked	Dimethylformamide	Common solvents
Polyoxymethylene	Insoluble	All solvents
Poly(ethylene oxide)	Alcohols, chlorinated hydrocarbons water	Petroleum ether
Epoxy resins		
Uncured	Alcohols, ketones, esters, dioxane, benzene, methylene chloride	Aliphatic hydrocarbons, water
Cured	Practically insoluble	
Cellulose, regenerated	Schweizer's reagent	Organic solvents
Cellulose ethers		
Methyl	Water, dil. Sodium hydroxide	Organic solvents
Ethyl	Methanol, methylene chloride	Water, aliphatic and aromatic hydrocarbons
Cellulose esters (acetate, propionate)	Ketons, esters	Aliphatic hydrocarbons
Cellulose nitrate	Esters (ethyl acetate, butyl acetate, etc.), ketones (acetone, methyl ethyl ketone, etc.), mixtures (eg. 80% methyl isobutyl ketone + 20% isopropyl alcohol, 80% butyl acetate + 20% isopropyl alcohol)	Aliphatic hydrocarbons (hexane, heptane, etc.) methyl alcohol, water
Natural rubber	Aromatic hydrocarbons, chlorinated hydrocarbons	Petroleum ether, alcohols ketones, esters
Chlorinated rubber	Esters, ketones, linseed oil (80–100°C), carbon tetrachloride, tetrahydrofuran	Aliphatic hydrocarbons
Styrene-butadiene rubber	Ethyl acetate, benzene, methylene chloride	Alcohols, water

Source: From Krause, A. and Lange, A. 1969. *Introduction to Chemical Analysis of Plastics*. Iliffe Books Ltd., London.

For urea, solution 1 remains colorless and solution 2 becomes orange to red after 3–5 h. For melamine, solution 1 slowly becomes orange and solution 2 remains colorless.

Detection of urea with urease also provides a useful differentiation between urea and melamine resins. For this test, the powdered sample (0.25 g) is placed in a 100 ml Erlenmeyer flask and boiled with 5% sulphuric acid until the smell of formaldehyde has disappeared. The mixture is neutralized with sodium hydroxide (phenolphthalein as indicator). Then 1 drop of 1 N sulphuric acid and 10 ml of 10% urease solution is added, a strip of red litmus paper is placed in the vapors and the flask is stoppered. The appearance of a blue color in the litmus paper after a short time indicates urea and thus the presence of urea resin.

8. *Test for cellulose esters.* Cellulose esters respond to the Molisch test for carbohydrates. The sample is dissolved in acetone and treated with 2–3 drops of 2% ethanolic solution of α -naphthol; a volume of 2–2.5 ml of concentrated H_2SO_4 is so added as to form a lower layer. A red to red–brown ring at the interface of the liquids indicates cellulose (glucose). A green ring at the interface indicates nitrocellulose and differentiates it from other cellulose esters.

A more sensitive test for nitrocellulose is provided by an intense blue color reaction when a drop of a solution of diphenylamine in concentrated H_2SO_4 (5% w/v) is added to the sample in the absence of other oxidizing agents.

9. *Test for polyamides.* When a strip of filter paper soaked in a fresh saturated solution of *o*-nitrobenzaldehyde in dilute sodium hydroxide is held over the pyrolytic vapors of polyamides containing adipic acid, a mauve-black color is readily developed. Pyrolytic vapors of polyamides from diacids other than adipic acid produce a grey color when tested similarly.
10. *Tests for natural rubber and synthetic rubbers.* Rubbers may be identified by testing the pyrolytic vapors from test samples. A strip of filter paper soaked in an ethereal solution containing *p*-dimethylaminobenzaldehyde (3%) and hydroquinone (0.05%) and then moistened with a 30% solution of trichloroacetic acid in isopropanol produces different color reactions in the presence of pyrolytic vapors of different rubbers.

Vapors from natural rubber (NR) produce a deep blue or blue-violet color, and those from styrene-butadiene rubber (SBR) pyrolysis turn the paper green or blue with a distinct green tinge. Polyisobutylenes and butyl rubber resemble NR, and silicone rubbers resemble SBR, in this color reaction. Pyrolytic vapors from nitrile rubbers, on the other hand, give a brown or brown-yellow color and those from polychloroprenes (neoprene) turn the test paper grey with a yellow tinge.

In another test, pyrolytic vapors from polyisobutylenes and butyl rubbers produce a bright yellow color on filter paper freshly soaked in a solution obtained by dissolving yellow mercuric oxide (5 g) in concentrated sulfuric acid (15 ml) and water (85 ml) on boiling. Other rubbers may either produce little change or give an uncharacteristic brown color.

Chromic acid oxidation provides a simple test for polyisoprenes. About 0.1 g of sample is gently heated in a test tube in the presence of chromic acid solution (5 ml) prepared by dissolving chromium trioxide (2 g) in water (5 ml) and adding concentrated sulfuric acid (1.5 ml). 1,4-Polyisoprenes (the synthetic equivalent of natural rubber) yield acetic acid, which can be readily identified by its odor.

If the above test is positive, the sample may be further subjected to a modified Weber color test for polyisoprenes. For this test, an acetone-extracted polymer (0.05 g) is dissolved or suspended in carbon tetrachloride, treated with a little solution of bromine in carbon tetrachloride and heated in a water bath to remove excess bromine. The residue is then warmed with a little phenol. In the presence of polyisoprenes, the solid or the solution turns violet or purple and gives a purple solution with chloroform. The test is also positive for natural rubber and butyl rubber.

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Industrial Polymers

4.1 Introduction

The first completely synthetic plastic, phenol-formaldehyde, was introduced by L. H. Baekeland in 1909, nearly four decades after J. W. Hyatt had developed a semisynthetic plastic—cellulose nitrate. Both Hyatt and Baekeland invented their plastics by trial and error. Thus the step from the idea of macromolecules to the reality of producing them at will was still not made. It had to wait till the pioneering work of Hermann Staudinger, who, in 1924, proposed linear molecular structures for polystyrene and natural rubber. His work brought recognition to the fact that the macromolecules really are linear polymers. After this it did not take long for other materials to arrive. In 1927 poly(vinyl chloride) (PVC) and cellulose acetate were developed, and 1929 saw the introduction of urea-formaldehyde (UF) resins.

The production of nylon-6,6 (first synthesized by W. H. Carothers in 1935) was started by Du Pont in 1938, and the production of nylon-6 (perlon) by I. G. Farben began in 1938, using the caprolactam route to nylon developed by P. Schlock. The latter was the first example of ring-opening polymerization. The years prior to World War II saw the rapid commercial development of many important plastics, such as acrylics and poly(vinyl acetate) in 1936, polystyrene in 1938, melamine-formaldehyde (formica) in 1939, and polyethylene and polyester in 1941. The amazing scope of wartime applications accelerated the development and growth of polymers to meet the diverse needs of special materials in different fields of activity.

The development of new polymeric materials proceeded at an even faster pace after the war. Epoxies were developed in 1947, and acrylonitrile-butadiene-styrene (ABS) terpolymer in 1948. The polyurethanes, introduced in Germany in 1937, saw rapid development in the United States as the technology became available after the war. The discovery of Ziegler-Natta catalysts in the 1950s brought about the development of linear polyethylene and stereoregular polypropylene. These years also saw the emergence of acetal, polyethylene terephthalate, polycarbonate, and a host of new copolymers. The next two decades saw the commercial development of a number of highly temperature-resistant materials, which included poly(phenylene oxide) (PPO), polysulfones, polyimides, polyamide-imides, and polybenzimidazoles.

Numerous plastics and fibers are produced from synthetic polymers: containers from polypropylene, coating materials from PVC, packaging film from polyethylene, experimental apparatus from Teflon, organic glasses from poly(methyl methacrylate), stockings from nylon fiber—there are simply too many to mention them all. The reason why plastics materials are popular is that they may offer such advantages as transparency, self-lubrication, lightweight, flexibility, economy in fabricating, and decorating.

Properties of plastics can be modified through the use of fillers, reinforcing agents, and chemical additives. Plastics have thus found many engineering applications, such as mechanical units under stress, low-friction components, heat- and chemical-resistant units, electrical parts, high-light-transmission applications, housing, building construction functions, and many others. Although it is true that in these applications plastics have been used in a proper manner according to our needs, other ways of utilizing both natural and synthetic polymers may still remain. To investigate these further possibilities, active

research has been initiated in a field called *specialty polymers*. This field relates to synthesis of new polymers with high additional value and specific functions.

Many of the synthetic plastic materials have found established uses in a number of important areas of engineering involving mechanical, electrical, telecommunication, aerospace, chemical, biochemical, and biomedical applications. There is, however, no single satisfactory definition of engineering plastics. According to one definition, engineering plastics are those which possess physical properties enabling them to perform for prolonged use in structural applications, over a wide temperature range, under mechanical stress and in difficult chemical and physical environments. In the most general sense, however, all polymers are engineering materials, in that they offer specific properties which we judge quantitatively in the design of end-use applications.

For the purpose of this discussion, we will classify polymers into three broad groups: addition polymers, condensation polymers, and special polymers. By convention, polymers whose main chains consist entirely of C–C bond are *addition polymers*, whereas those in which hetero atoms (e.g., O, N, S, Si) are present in the polymer backbone are considered to be *condensation polymers*. Grouped as *special polymers* are those products which have special properties, such as temperature and fire resistance, photosensitivity, electrical conductivity, and piezoelectric properties, or which possess specific reactivities to serve as functional polymers.

Further classification of polymers in the groups of additional polymers and condensation polymers has been on monomer composition, because this provides an orderly approach, whereas classification based on polymer uses, such as plastics, elastomers, fibers, coatings, etc. would result in too much overlap. For example, polyamides are used not only as synthetic fibers but also as thermoplastics molding compounds and polypropylene, which is used as a thermoplastic molding compound has also found uses as a fiber-forming material.

All vinyl polymers are addition polymers. To differentiate the, the homopolymers have been classified by the substituents attached to one carbon atom of the double bone. If the substituent is hydrogen, alkyl or aryl, the homopolymers are listed under polyolefins. Olefin homopolymers with other substituents are described under *polyvinyl* compounds, except where the substituent is a nitrile, a carboxylic acid, or a carboxylic acid ester or amide. The monomers in the latter cases being derivatives of acrylic acid, the derived polymers are listed under *acrylics*. Under olefin copolymers are listed products which are produced by copolymerization of two or more monomers.

Condensation polymers are classified as polyesters, polyamides, polyurethanes, and ether polymers, based on the internal functional group being ester (–COO–), amide (–CONH–), urethane (–OCONH–), or ether (–O–). Another group of condensation polymers derived by condensation reactions with formaldehyde is described under formaldehyde resins. Polymers with special properties have been classified into three groups: heat-resistant polymers, silicones and other inorganic polymer, and functional polymers. Discussions in all cases are centered on important properties and main applications of polymers.

4.2 Part I: Addition Polymers

Addition polymers are produced in largest tonnages among industrial polymers. The most important monomers are ethylene, propylene, and butadiene. They are based on low-cost petrochemicals or natural gas and are produced by cracking or refining of crude oil. Polyethylene, polypropylene, poly(vinyl chloride), and polystyrene are the four major addition polymers and are by far the least-expensive industrial polymers on the market. In addition to these four products, a wide variety of other addition polymers are commercially available.

For addition polymers four types of polymerization processes are known: free-radical-initiated chain polymerization, anionic polymerization, cationic polymerization, and coordination polymerization (with Ziegler–Natta catalysts). By far the most extensively used process is the free-radical-initiated chain polymerization. However, the more recent development of stereo regular polymers using certain

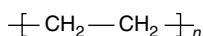
organometallic coordination compounds called Ziegler–Natta catalysts, which has added a new dimension to polymerization processes, is expected to play a more important role in coming years. The production of linear low-density polyethylene (LLDPE) is a good example. Ionic polymerization is used to a lesser extent. Thus, anionic polymerization is used mainly in the copolymerization of olefins, such as the production of styrene–butadiene elastomers, and cationic polymerization is used exclusively in the production of butyl rubber.

Different processes are used in industry for the manufacture of polymers by free-radical chain polymerization. Among them *homogeneous bulk polymerization* is economically the most attractive and yields products of higher purity and clarity. But it has problems associated with the heat of polymerization, increases in viscosity, and removal of unreacted monomer. This method is nevertheless used for the manufacture of PVC, polystyrene, and poly(methyl methacrylate). More common processes are *homogeneous solution polymerization* and *heterogeneous suspension polymerization*.

Solution polymerization is used for the manufacture of polyethylene, polypropylene, and polystyrene, but by far the most widely used process for polystyrene and PVC is suspension polymerization. In the latter process (also known as *bead*, *pearl*, or *granular polymerization* because of the form in which the final products may be obtained), the monomer is dispersed as droplets (0.01–0.05 cm in diameter) in water by mechanical agitation. Various types of stabilizers, which include water-soluble organic polymers, electrolytes, and water-insoluble inorganic compounds, are added to prevent agglomeration of the monomer droplets. Each monomer droplet in the suspension constitutes a small bulk polymerization system and is transformed finally into a solid bead. Heat of polymerization is quickly dissipated by continuously stirring the suspension medium, which makes temperature control relatively easy.

4.2.1 Polyolefins

4.2.1.1 Polyethylene



Monomer	Polymerization	Major Uses
Ethylene	LDPE: free-radical-initiated chain polymerization	LDPE: film and sheet (55%), housewares and toys (16%), wire and cable coating (5%)
	HDPE: Ziegler–Natta or metal-oxide catalyzed chain polymerization	HDPE: bottles (40%), housewares, containers, toys (35%), pipe and fittings (10%), film and sheet (5%)

Polyethylene is the most widely used thermoplastic material and is composed of ethylene. The two main types are LDPE and high-density polyethylene (HDPE) [1].

4.2.1.1.1 Manufacturing Processes

LDPE is manufactured by polymerization of ethylene under high pressures (15,000–50,000 psi, i.e., 103–345 MPa) and elevated temperatures (200–350°C) in the presence of oxygen (0.03–0.1%) as free-radical initiator. Ethylene is a supercritical fluid with density 0.4–0.5 g/cm³ under these conditions. Polyethylene remains dissolved in ethylene at high pressures and temperatures but separates in the lower ranges. Branch polyethylene is produced due to chain transfer to polymer. The type and extent of branching depends on the local reaction temperature and concentrations of monomer and polymer. The molecular weight distributions and the frequencies of long and short branches on polymer chains depend strongly on reactor geometry and operation. The branched products (LDPE) are less crystalline and rigid than higher density species (HDPE) made by low pressure coordination polymerization.

Linear polyethylenes are produced in solution, slurry, and increasingly, gas-phase low-pressure processes. The Phillips process developed during the mid 1950s used supported chromium trioxide catalysts in a continuous slurry process (or particle-form process) carried out in loop reactors. Earlier, Standard Oil of Indiana patented a process using a supported molybdenum oxide catalyst. The polyethylenes made by both these processes are HDPE with densities of 0.950–0.965 g/cm³ and they are linear with very few side-chain branches and have a high degree of crystallinity.

During the late 1970s, Union Carbide developed a low-pressure polymerization process (Unipol process) capable of producing polyethylene in the gas phase that required no solvents. The process employed a chromium based catalyst. In this process (Figure 4.1) ethylene gas and solid catalysts are fed continuously to a fluidized bed reactor. The fluidized material is polyethylene powder which is produced as a result of polymerization of the ethylene on the catalyst. The ethylene, which is recycled, supplies monomer for the reaction, fluidizes the solid, and serves as a heat-removal medium. The reaction is exothermic and is normally run at temperatures 25–50°C below the softening temperatures of the polyethylene powder in the bed. This operation requires very good heat transfer to avoid hot spots and means that the gas distribution and fluidization must be uniform.

The keys to the process are active catalysts. These are special organochromium compounds on particular supports. The catalysts yield up to about 10⁶ kg of polymer per kilogram of metallic chromium. Branching is controlled by the use of comonomers like propylene or 1-butene, and hydrogen is used as a chain transfer agent. The catalyst is so efficient that its concentration in the final product is negligible. The absence of a solvent and a catalyst removal step makes the process less expensive. The products marketed as linear LLDPE can be considered as linear polyethylenes having a significant number of branches (pendant alkyl groups). The linearity imparts strength, the branches impart toughness.

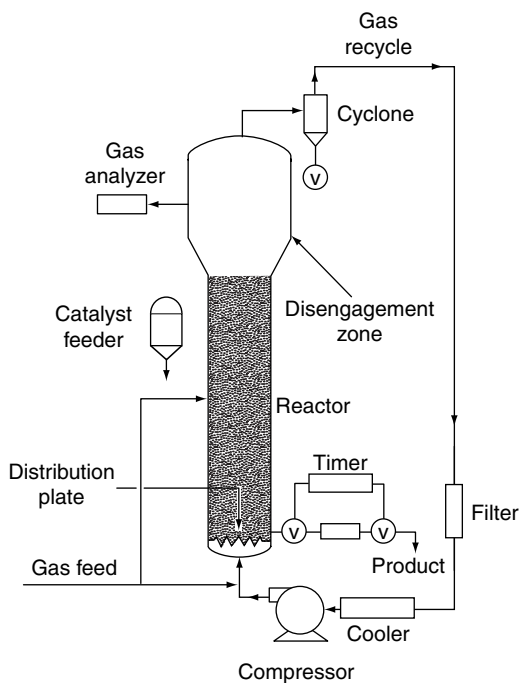


FIGURE 4.1 Union Carbide gas phase process for the production of polyethylene.

TABLE 4.1 Types of Polyethylene

Material	Chain Structure	Density (g/cm ³)	Crystallinity (%)	Process
LDPE	Branched	0.912–0.94	50	High pressure
LLDPE	Linear/less branched	0.92–0.94	50	Low pressure
HDPE	Linear	0.958	90	Low pressure

During the late 1970s, the Dow Chemical Co. also began producing polyethylene using a proprietary solution process based on Ziegler–Natta-type catalysts. Resins are made at low pressures and with lower densities in a system derived essentially from high-density resin technology (Ziegler–Natta). Higher boiling comonomers (1-hexene and 1-octene) are used to produce LLDPE having superior mechanical properties and film-drawing tendencies. A difference of the Dow solution products from gas-phase products is that they are produced in standard pellet form with any needed additives incorporated into the pellet.

Polyethylene is partially amorphous and partially crystalline. Linearity of polymer chains affords more efficient packing of molecules and hence a higher degree of crystallinity. On the other hand, side-chain branching reduces the degree of crystallinity. Increasing crystallinity increases density, stiffness, hardness, tensile strength, heat and chemical resistance, creep resistance, barrier properties, and opacity, but it reduces stress-crack resistance, permeability, and impact strength. Table 4.1 shows a comparison of three types of polyethylene.

Polyethylene has excellent chemical resistance and is not attacked by acids, bases, or salts. (It is, however, attacked by strong oxidizing agents.) The other characteristics of polyethylene which have led to its widespread use are low cost, easy process ability, excellent electrical insulation properties, toughness and flexibility even at low temperatures, freedom from odor and toxicity, reasonable clarity of thin films, and sufficiently low permeability to water vapor for many packaging, building, and agricultural applications.

Major markets for LDPE are in packaging and sheeting, whereas HDPE is used mainly in blow-molded products (milk bottles, household and cosmetic bottles, fuel tanks), and in pipe, wire, and cable applications. Ultra-high-molecular-weight polyethylene materials (see later), which are the toughest of plastics, are doing an unusual job in the textile machinery field.

4.2.1.1.2 Chlorinated Polyethylene

Low chlorination of polyethylene, causing random substitution, reduces chain order and thereby also the crystallinity. The low chlorine products (22–26% chlorine) of polyethylene are softer, more rubber-like, and more compatible and soluble than the original polyethylene. However, much of the market of such materials has been taken up by chlorosulfonated polyethylene (Hypalon, Du Pont), produced by chlorination of polyethylene in the presence of sulfur dioxide, which introduces chlorosulfonyl groups in the chain.

Chlorosulfonated LDPE containing about 27% chlorine and 1.5% sulfur has the highest elongation. Chlorosulfonated polyethylene rubbers, designated as CSM rubbers, have very good heat, ozone, and weathering resistance together with a good resistance to oils and a wide spectrum of chemicals. The bulk of the output is used for fabric coating, film sheeting, and pit liner systems in the construction industry, and as sheathing for nuclear power cables, for offshore oil rig cables, and in diesel electric locomotives.

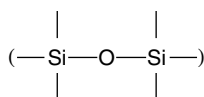
4.2.1.1.3 Cross-Linked Polyethylene

Cross-linking polyethylene enhances its heat resistance (in terms of resistance to melt flow) since the network persists even about the crystalline melting point of the uncross-linked material. Cross-linked polyethylene thus finds application in the cable industry as a dielectric and as a sheathing material. Three main approaches used for cross-linking polyethylene are (1) radiation cross-linking, (2) peroxide cross-linking, and (3) vinyl silane cross-linking.

Radiation cross-linking is most suitable for thin sections. The technique, however, requires expensive equipment and protective measure against radiation. Equipment requirements for peroxide curing are simpler, but the method requires close control. The peroxide molecules break up at elevated temperatures, producing free radicals which then abstract hydrogen from the polymer chain to produce a polymer free radical. Two such radicals can combine and thus cross-link the two chains. It is important, however, that the peroxide be sufficiently stable thermally so that premature cross-linking does not take place during compounding and shaping operations. Dicumyl peroxide is often used for LDPE but more stable peroxides are necessary for HDPE. For cross-linking polyethylene in cable coverings, high curing temperatures, using high-pressure steam in a long curing tube set into the extrusion line, are normally employed.

Copolymers of ethylene with a small amount of vinyl acetate are often preferred for peroxide cross-linking because the latter promotes the cross-linking process. Large amounts of carbon black may be incorporated into polyethylene that is to be cross-linked. The carbon black is believed to take part in the cross-linking process, and the mechanical properties of the resulting product are superior to those of the unfilled material.

In the vinyl silane cross-linking process (*Sioplas process*) developed by Dow, an easily hydrolysable trialkoxy vinyl silane, $\text{CH}_2=\text{CHSi}(\text{OR})_3$, is grafted onto the polyethylene chain, the site activation having been achieved with the aid of a small amount of peroxide. The material is then extruded onto the wire. When exposed to hot water or low-pressure steam, the alkoxy groups hydrolyze and then condense to form a siloxane cross-link:



The cross-linking reaction is facilitated by the use of a cross-linking catalyst, which is typically an organotin compound. There are several variations of the silane cross-linking process. In one process, compounding, grafting, and extrusion onto wire are carried out in the same extruder.

Cross-linked LDPE foam (see 'Polyolefin Foams' in [Chapter 2](#)) has been produced by using either chemical cross-linking or radiation cross-linking. These materials have been used in the automotive industry for carpeting, boot mats, sound deadening, and pipe insulation, and as flotation media for oil-carrying and dredging hose.

4.2.1.1.4 Linear Low-Density Polyethylene

Chemically, LLDPE can be described as linear polyethylene copolymers with alpha-olefin comonomers in the ethylene chain. They are produced primarily at low pressures and temperatures by the copolymerization of ethylene with various alpha-olefins such as butene, hexane, octane, etc., in the presence of suitable catalysts. Either gas-phase fluidized-bed reactors or liquid-phase solution-process reactors are used. (In contrast, LDPE is produced at very high pressures and temperatures either in autoclaves or tubular reactors.)

Polymer properties such as molecular weight, molecular-weight distribution (MWD), crystallinity, and density are controlled through catalyst selection and control of reactor conditions. Among the LLDPE processes, the gas-phase process has shown the greatest flexibility to produce resins over the full commercial range.

The molecular structure of LLDPE differs significantly from that of LDPE: LDPE has a highly branched structure, but LLDPE has the linear molecular structure of HDPE, though it has less crystallinity and density than the latter (see [Table 4.1](#)).

The stress-crack resistance of LLDPE is considerably higher than that of LDPE with the same melt index and density. Similar comparisons can be made with regard to puncture resistance, tensile strength, tensile elongation, and low- and high-temperature toughness. Thus LLDPE allows the processor to make a stronger product at the same gauge or an equivalent product at a reduced gauge.

LLDPE is now replacing conventional LDPE in many architectures because of the combination of favorable production economics and product performance characteristics. For many architectures (blow molding, injection molding, rotational molding, etc.) existing equipment for processing LDPE can be used to process LLDPE. LLDPE film can be treated, printed, and sealed by using the same equipment used for LDPE. Heat-sealing may, however, require slightly higher temperatures.

LLDPE films provide superior puncture resistance, high tensile strength, high impact strength, and outstanding low-temperature properties. The resins can be drawn down to thicknesses below 0.5 mil without bubble breaks. Slot-cast films combine high clarity and gloss with toughness. LLDPE films are being increasingly used in food packaging for such markets as ice bags and retail merchandise bags, and as industrial liners and garment bags.

Good flex properties and environmental stress-crack resistance combined with good low-temperature impact strength and low warp age make LLDPE suitable for injection-molded parts for housewares, closures, and lids. Extruded pipe and tubing made from LLDPE exhibit good stress-crack resistance and good bursting strength.

Blow-molded LLDPE parts such as toys, bottles, and drum liners provide high strength, flex life, and stress-crack resistance. Light-weight parts and faster blow-molding cycle times can be achieved. The combination of good high- and low-temperature properties, toughness, environmental stress-crack resistance, and good dielectric properties suit LLDPE for wire and cable insulation and jacketing applications.

A new class of linear polyethylene copolymers with densities ranging between 0.890 and 0.915 g/cm³, known as *very low-density polyethylene* (VLDPE), was introduced commercially in late 1984 by Union Carbide. These resins are produced by copolymerization of ethylene and alpha-olefins in the presence of a catalyst.

VLDPE provides flexibility previously available only in lower-strength materials, such as ethylene-vinyl acetate (EVA) copolymer (see later) and plasticized PVC, together with the toughness and broader operating temperature range of LLDPE. Its unique combination of properties makes VLDPE suited for a wide range of applications.

Generally, it is expected that VLDPE will be widely used as an impact modifier. Tests suggest that it is suited as a blending resin for polypropylene and in HDPE films for improved tear strength.

On its own, VLDPE should find use in applications requiring impact strength, puncture resistance, and dart drop resistance combined with flexibility. The drawdown characteristics of VLDPE allow for very thin films to be formed without pinholing. Soft flexible films for disposable gloves, furniture films, and high-performance stretch and shrink film are potential markets.

4.2.1.1.5 High-Molecular-Weight High-Density Polyethylene

High-molecular-weight high-density polyethylene (HMW-HDPE) is defined as a linear homopolymers or copolymer with a weight-average molecular weight (\bar{M}_w) in the range of approximately 200,000–500,000. HMW-HDPE resins are manufactured using predominantly two basic catalyst systems: Ziegler-type catalysts and chromium oxide-based catalysts. These catalysts produce linear polymers which can be either homopolymers when higher-density products are required or copolymers with lower density. Typical comonomers used in the latter type of products are butene, hexane, and octenes.

HMW-HDPE resins have high viscosity because of their high molecular weight. This presents problems in processing and, consequently, these resins are normally produced with broad MWD.

The combination of high molecular weight and high density imparts the HMW-HDPE good stiffness characteristics together with above-average abrasion resistance and chemical resistance. Because of the relatively high melting temperature, it is imperative that HMW-HDPE resins be specially stabilized with antioxidant and processing stabilizers. HMW-HDPE products are normally manufactured by the extrusion process; injection molding is seldom used.

The principal applications of HMW-HDPE are in film, pressure pipe, large blow-molded articles, and extruded sheet. HMW-HDPE film now finds application in T-shirt grocery sacks (with 0.6–0.9-mil thick

sacks capable of carrying 30 lb of produce), trash bags, industrial liners, and specialty roll stock. Sheets 20–100 mils thick and 18–20 ft wide are available that can be welded in situ for pond and tank liners.

HMW-HDPE piping is used extensively in gas distribution, water collection and supply, irrigation pipe, industrial effluent discharge, and cable conduit. The availability of pipe materials with significantly higher hydrostatic design stress (800 psi compared with 630 psi of the original HDPE resins) has given added impetus to their use. Large-diameter HMW-HDPE piping has found increasing use in sewer relining.

Large-blow-molded articles, such as 55-gal shipping containers, are produced. Equipment is now available to blow mold very large containers, such as 200- and 500-gal capacity industrial trash receptacles and 250-gal vessels to transport hazardous chemicals.

4.2.1.1.6 Ultrahigh-Molecular-Weight Polyethylene

Ultrahigh-molecular-weight polyethylene (UHMWPE) is defined by ATM as “polyethylene with molecular weight over three million (weight average).” The resin is made by a special Ziegler-type polymerization.

Being chemically similar to HDPE, UHMWPE shows the typical polyethylene characteristics of chemical inertness, lubricity, and electrical resistance, while its very long substantially linear chains provide greater impact strength, abrasion resistance, toughness, and freedom from stress cracking. However, this very high molecular weight also makes it difficult to process the polymer by standard molding and extrusion techniques. Compression molding of sheets and ram extrusion of profiles are the normal manufacturing techniques.

Forms produced by compression molding or specialty extrusion can be made into final form by machining, sintering, or forging. Standard wood-working techniques are employed for machining; sharp tools, low pressures, and good cooling are used. Forging can be accomplished by pressing a perform and billet and then forging to then final shape. Parts are also formed from compression-molded or skived sheets by heating them above 300°F ($\sim 150^{\circ}\text{C}$) and stamping them in typical metal-stamping equipment. Such UHMWPE items have better abrasion resistance than do steel or polyurethanes. They also have high impact strength even at very low temperatures, high resistance to cyclic fatigue and stress cracking, low coefficient friction, good corrosion and chemical resistance, good resistance to nuclear radiation, and resistance to boiling water.

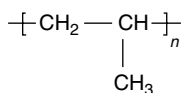
Fillers such as graphite, talc, glass beads or fibers, mica, and powdered metals can be incorporated to improve stiffness or to reduce deformation and deflection under load. Resistance to abrasion and deformation can be increased by peroxide cross-linking, described earlier.

UHMWPE was first used in the textile machinery field picker blocks and throw sticks, for example. Wear strips, timing wheels, and gears made of the UHMW polymer are used in material handling, assembly, and packaging lines. Chemical resistance and lubricity of the polymer are important in its applications in chemical, food, beverage, mining, mineral processing, and paper industries. All sorts of self-unloading containers use UHMWPE liners to reduce wear, prevent sticking, and speed up the unloading cycles. The polymer provides slippery surfaces that facilitate unloading even when the product is wet or frozen.

The polymer finds applications in transportation, recreation, lumbering, and general manufacturing. Metal equipment parts in some cases are coated or replaced with UHMWPE parts to reduce wear and prevent corrosion. Sewage plants have used this polymer to replace cast-iron wear shoes and rails, bearings, and sprockets. There is even an effort to use UHMW polymer chain to replace metal chain, which is corroded by such environments.

Porous UHMW polymer is made by sintering to produce articles of varied porosity. It has found growing use for controlled-porosity battery separators. Patents have been issued on the production of ultrahigh strength, very lightweight fibers from UHMW polymer by gel spinning.

4.2.1.2 Polypropylene



Monomer	Polymerization	Major Uses
Propylene	Ziegler–Natta catalyzed chain polymerization	Fiber products (30%), housewares and toys (15%), automotive parts (15%), appliance parts (5%)

Since its conception in the late 1950s, the propylene polymerization is being revolutionized in terms of both manufacturing hardware and, more importantly, catalyst technology [2–4]. New catalyst technologies, in conjunction with state-of-the-art polymerization, have established polypropylene as the kingpin in the field of polyolefins. A brief survey of manufacturing processes and catalyst technologies are presented below.

4.2.1.2.1 Manufacturing Processes

Commercial production of crystalline polypropylene (PP) was first put on stream in late 1959 by Hercules in the United States, by Montecatini in Italy, and by Farbenwerke Hoechst AG in Germany. The workhorse process for commercial production of PP has been slurry polymerizations in liquid hydrocarbon diluent, for example, hexane or heptane. These are carried out either in stirred batch or continuous reactors.

High purity (>99.5%) propylene is fed to the reactor containing diluent, as a suspension of solid (Ziegler–Natta) catalyst particles is metered in. The reaction is carried out at 50–80°C and 5–20 atmospheric pressure. The crystalline polymer produced is insoluble and forms a finely divided granular solid enveloping the solid catalyst particles. Monomer addition is continued until the slurry reaches 20–40% solids. Residence time varies from minutes to several hours, depending on the catalyst concentration and activity, as well as the specific reaction conditions. Molecular weight is controlled preferentially by the addition of hydrogen as the chain transfer agent.

The reactor slurry of PP is discharged to a stripping unit where the unreacted monomer flashes out for recycling. The catalyst is then deactivated and solubilized by the addition of alcohol. The bulk of the diluent, solubilized catalysts, and atactic polypropylene in solution are removed at this point by centrifuging. The crystalline polymer is purified by steam distillation and/or by water washing with surface active agents, followed by filtration and centrifuging and then drying. The dried polymer can be stored, transported, or premixed with stabilizers to be used with or without pelletization.

The efficiency of the Ziegler–Natta catalysts is of the order of 1500 g polymer formed per gram of transition metal. Residual catalyst has adverse effects on the corrosiveness, color, and light stability of the polymer, and extraction processes must be used to remove it from the product. However, by utilizing state-of-the-art, high-mileage (supported) catalyst systems, polymer yields are obtained which are several orders of magnitude higher than those obtained with first generation, Ziegler catalysts. Typically the high-mileage catalysts produce about 300,000 g of polymer per gram of transition metal. Since there are only about 3 ppm of residual metal in the polymer, catalyst removal is unnecessary. The expensive catalyst removal (deashing) steps required for the products made by earlier Ziegler catalyst systems are thus eliminated.

Propylene is readily polymerized in bulk; that is, in the liquid monomer itself. Arco, El Paso, Phillips, and Shell are practitioners of bulk processing in stirred or loop reactor systems. In either case, liquid propylene (and ethylene, if random copolymer is desired) is continuously metered to the polymerization reactor along with a high-activity/high-stereospecificity catalyst system. Polymerization temperatures are normally in the range of 45–80°C with pressures sufficient to maintain propylene in the liquid phase

(250–500 psi, that is, 1.7–3.5 MPa). Hydrogen is used for molecular weight control. The polymer slurry (approximately 30–50% solids in liquid propylene) is continuously discharged from loop reactors through a series of sequence valves into a zone maintained essentially at atmospheric pressure and containing terminating agents. Technologies also exist for production of propylene/ethylene block copolymers via bulk polymerization employing stirred or loop reactors [5].

Modern vapor-phase polymerization is represented in one form by the stirred gas-phase process originally developed by BASF and licensed by Norchem in the United States [6]. BASF process reactors contain a spiral or double-helical agitator to stir the polymer bed. Cooling of the bed is maintained by continuous injection of fresh, high-purity propylene in a liquid or partly liquefied state into the reaction zone. The unreacted propylene is removed from the top of the reactor during polymerization, condensed, and reinjected with fresh propylene. Evaporation of the unreacted propylene absorbs the heat of polymerization and also brings about intense mixing of the solid polymer particles with the gas phase. Energy costs of the process are economically attractive [7]. The diluent-free BASF process provides sufficiently high yield of polymer per unit of catalyst so that deashing is not required. Although products made in this way contain relatively high levels of titanium and aluminum residues, a unique finishing step during extrusion palletizing reduces active chlorides to an innocuous level [6].

With dramatic improvements in Ziegler–Natta catalyst technology, the *Spheripol process*, first developed by Montedison and Mitsui Petrochemical with simplified bulk (liquid propylene) process technology operating with loop reactors, is capable of directly producing a relatively large round bead with suitable density to eliminate the need for pelletizing for many applications [5]. Subsequently, Montedison and Hercules, Inc., which assumed responsibility for all polypropylene operations and technology of the parent companies.

The Himont spheripol loop reactor process is initiated by injecting specially prepared supported catalyst and cocatalyst into liquid propylene circulated in a relatively simply high L/D ratio loop reactor, followed by monomer removal (Figure 4.2). The homopolymers so produced can be circulated through ethylene and ethylene/propylene gas phase reactors for insertion of copolymer fractions before final monomer stripping.

The Unipol low-pressure gas-phase fluidized-bed process, which was introduced by Union Carbide in 1977 for LLDPE, has also been adapted to the production of PP homopolymers and block copolymers using Shell Chemicals high-activity (Ziegler-type) catalyst technology. The Spheripol and Unipol

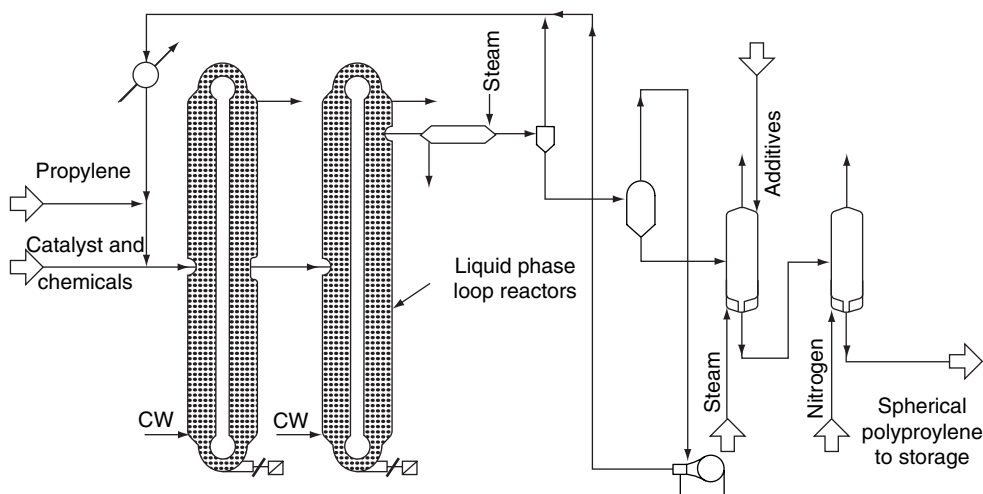


FIGURE 4.2 A simplified flow diagram of the Himont spheripol loop reactor process.

processes are capable of producing polymer in crumb bead or granular forms, with the potential for direct marketing without any pelletizing finishing operation.

Regardless of the polymerization process used, the PP homo- and co-polymer must be stabilized to some degree to prevent oxidative degradation. The general practice is to incorporate a small quantity of stabilizer in the polymer prior to the first exposure to elevated temperatures of a drying operation or long-term storage. Inert-gas (nitrogen) blanketing is also used in some storage/transfer systems. Additional stabilizers, up to 1%, are added to the polymer during pelletizing. Most commercial PP compositions contain mixtures of hindered phenols and hydroperoxide decomposers or various phosphates (see [Chapter 1](#)).

4.2.1.2.2 Catalyst Technology

The origin of sophisticated catalyst used today are to be found in the early work of Karl Ziegler (1950) and Giulio Natta (1954). In the last five decades, several distinct “generations” of catalyst technologies have emerged. The earliest commercial catalysts (*first generation*) were essentially titanium trichloride, simply prepared by reducing TiCl_4 with alkylaluminums to yield brown (β) TiCl_3 , which was subsequently heated to convert it to the stereospecific purple (γ) form.

In the 1970s, improved or *second-generation catalysts* were developed. The essence of the improvement was that catalyst poisons AlCl_3 or AlEtCl_2 , which are cocrystallized with or absorbed onto the TiCl_3 catalyst, were removed by using dialkyl ethers (especially di-*n*-butyl ether and di-isoamyl ether).

The 1980s heralded the widespread commercial implementation of supported catalysts. These *third-generation catalysts* comprise of TiCl_4 on a specially prepared MgCl_2 support. Commercially available MgCl_2 is converted to “active MgCl_2 ” by treating with “activating agents,” which are electron donors (Lewis bases) such as ethyl benzoate, diisobutylphthalate, and phenyl triethoxy silane. These are also used in conjunction with the cocatalyst (trialkylaluminum) as a “selectivity control agent.”

While the first-generation catalysts were suitable for slurry process, in which polymerization occurs in a paraffinic solvent, third-generation supported catalysts with dramatically higher activity (typically 1500 kg PP/g Ti compared to 15 kg/g Ti for first generation TiCl_3 catalyst) and stereo-specificity not only allowed the full exploitation of the advantages of a solventless polymerization, but also made substantial simplification of slurry process possible through elimination of atactic removal and catalyst de-ashing. These third-generation catalysts can be used in both the bulk and simplified slurry processes. They are, however, unsuitable for a gas-phase process.

The major advance offered by the later (*fourth generation*) supported catalysts is their controlled morphology, which rendered them suitable for all commercial polymerization processes. These are the only catalysts suitable for the full exploitation of the advantages of the solvent-less polymerization including the gas-phase process. These catalysts come in a variety of regular shapes, such as spherical, cubical, or cylindrical, as single particles or clusters of several particles, and are characterized by sufficiently narrow particle size distributions with the minimum of fines or coarse particles.

During polymerization, replication of the catalyst shape occurs, and hence spherical PP beads are obtained directly from the reactor, if the catalyst is spherical. By producing catalysts with a dense, spherical, and uniform particle shape it is thus possible to generate PP particles that, for many applications, can be shipped and used without a granulation or extrusion step to generate the “nibs” desired by most customers. This concept is already part of the Himont Spheripol process mentioned earlier.

While attractive in terms of economy, since the energy consuming extrusion step is obviated in the above process, there are various disadvantages such as the difficulty of homogeneously administering additives/stabilizers, the loss of the options for molecular weight modifications via extruder operation, and the fact that the process yields particles of smaller size than what is preferred by the industry simply because such large-size particles cannot be kept in suspension during polymerization.

Montecatini has developed spherical morphology MgCl_2 supported catalysts for ethylene and propylene polymerization. The name of this process is “spherilene.” The major advantage in such

The zirconium catalysts are three orders of magnitude more active than their titanium counterparts. Unlike the heterogeneous Ziegler–Natta catalysts in which usually several types of active catalyst sites are present, metallocene catalysts are *single-site* in nature, that is, they have a single active catalyst site on the catalyst structure and thus they make one type of polymer, ensuring a high degree of purity.

The very high selectivity of the zirconocene single-site catalysts and their high activity, which approaches that of the MgCl_2 -supported catalysts described in the previous section, makes them a serious contender for future processes. It can be expected [4] that the relative ease of tailoring of homogeneous catalysts compared to complicated heterogeneous systems will enable these catalysts to be further improved and exploited in terms of activity and selectivity (isotacticity, molecular weight, and distribution).

It is worthwhile to mention that homogeneous Ziegler–Natta catalysts other than metallocene-based catalysts have also been developing rapidly in recent years. The catalyst precursors of these systems are nonmetallocene organometallic compounds, such as monocyclopentadienyl derivatives. A representative of monocyclopentadienyl catalysts is the *constrained geometry (CG) catalyst*. This new type of homogeneous catalyst was developed by Dow Plastics [10]. The catalyst system is based on group IVB transition metals such as Ti, covalently bonded to a cyclopentadienyl group bridged with a heteroatom such as nitrogen. The components are linked in such a way that a constrained cyclic structure is formed with Ti at the center. The bond angle between the monocyclopentadienyl group, Ti center, and heteroatom is less than 115° . The catalyst is activated by strong Lewis acid systems to a highly efficient cationic form.

The CG catalysts produce highly processable polyolefins with a unique combination of narrow MWD and long chain branches. Ethylene–octene copolymers produced with CG catalysts have useful properties across a range of densities and melting indexes. These novel copolymer families are called *polyolefin plastomers* (POP) and *polyolefin elastomers* (POE). POPs possess plastic and elastic properties while POEs containing greater than 20 wt% octene comonomer units have higher elasticity.

The CG catalyst technology is not limited to the typical selection of C_2 – C_8 α -olefins, but can include higher α -olefins. The open structure of the CG catalyst significantly increases the flexibility to insert higher α -olefin comonomers into the polymer structure. This technology also allows addition of vinyl-ended polymer chains to produce long chain branching.

4.2.1.2.3 Properties

“Polypropylene” is not one or even 100 products. Rather it is a multidimensional range of products with properties and characteristics interdependent on the type of polymer (homopolymers, random, or block copolymer), molecular weight and molecular weight distribution, morphology and crystalline structure, additives, fillers and reinforcing fillers, and fabrication techniques.

Commercial homopolymers are usually about 90–95% isotactic, the other structures being atactic and syndiotactic (a rough measure of isotacticity is provided by the “isotactic index”—the percentage of polymer insoluble in heptane): the greater the degree of isotacticity the greater the crystallinity and hence the greater the softening point, stiffness, tensile strength, modulus, and hardness.

Although very similar to HDPE, PP has a lower density (0.90 g/cm^3) and a higher softening point, which enables it to withstand boiling water and many steam sterilizing operations. It has a higher brittle point and appears to be free from environmental stress-cracking problems, except with concentrated sulfuric acid, chromic acid, and aqua regia. However, because of the presence of tertiary carbon atoms occurring alternately on the chain backbone, PP is more susceptible to UV radiation and oxidation at elevated temperatures. Whereas PE cross-links on oxidation, PP undergoes degradation to form lower-molecular-weight products. Substantial improvement can be made by the inclusion of antioxidants, and such additives are used in all commercial PP compounds. The electrical properties of PP are very similar to those of HDPE.

Because of its reasonable cost and good combination of the foregoing properties, PP has found many applications, ranging from fibers and filament to films and extrusion coatings. A significant portion of the PP produced is used in moldings, which include luggage, stacking chairs, hospital sterilizable

equipment, toilet cisterns, washing machine parts, and various auto parts, such as accelerator pedals, battery cases, dome lights, kick panels, and door frames.

Although commercial PP is a highly crystalline polymer, PP moldings are less opaque when unpigmented than are corresponding HDPE moldings, because the differences between amorphous and crystal densities are less with PP (0.85 and 0.94 g/cm³, respectively) than with polyethylene (0.84 and 1.01 g/cm³, respectively).

A particularly useful property of PP is the excellent resistance of thin sections to continued flexing. This has led to the production of one-piece moldings for boxes, cases, and accelerator pedals in which the hinge is an integral part of the molding.

Monoaxially oriented polypropylene film tapes have been widely used for carpet backing and for woven sacks (replacing those made from jute). Combining strength and lightness, oriented PP straps have gained rapid and widespread acceptance for packaging.

Nonoriented PP film, which is glass clear, is used mainly for textile packaging. However, biaxially oriented PP film is more important because of its greater clarity, impact strength, and barrier properties. Coated grades of this material are used for packaging potato crisps, for wrapping bread and biscuits, and for capacitor dielectrics. In these applications PP has largely replaced regenerated cellulose. (The high degree of clarity of biaxially oriented PP is caused by layering of the crystalline structures. Layering reduces the variations in refractive index across the thickness of the film, which thus reduces the amount of light scattering.)

Polypropylene, produced by an oriented extrusion process, has been uniquely successful as a fiber. Its excellent wear, inertness to water, and microorganisms, and its comparatively low cost have made it extensively used in functional applications, such as carpet backing, upholstery fabrics, and interior trim for automobiles.

Random ethylene-propylene copolymers, another important variety of polypropylene, are noted for high clarity, a lower and broader melting range than homopolymers grades, reduced flexural modulus, and higher melt strengths. They are produced by the random addition of ethylene to a polypropylene chain as it grows. The melt-flow rate of random copolymers ranges from 1 g/10 min for a blow-molding grade to 35 g/10 min for an injection-molding grade. The density is about 0.90 g/cm³ and the notched Izod impact strength of the materials ranges from under 1 to more than 5 ft.-lb/in.

The blow-molded bottles capitalize on the good clarity provided by the random copolymer. The high gloss and very broad heat sealing range of this resin is useful in such cast-film applications as trading cards and document protectors. Polypropylene copolymers with a melt-flow rate of 35 g/10 min or above find applications in thin wall parts, usually for injection molded food packaging such as delicatessen containers or yogurt cups. Such containers have walls with a length-to-thickness ratio as high as 400:1; yet they retain the properties of top-load strength, impact resistance, and recyclability that are typical of polypropylene.

Block copolymers, preferably with ethylene, are classed as having medium, high, or extra-high impact resistance with particular respect to subzero temperatures. Block copolymers consist of a crystalline PP matrix containing segments of EPR-type elastomer and/or crystalline PE for energy impact absorption in the rubber phase [5]. The level of the ethylene comonomer as well as the size of these segments has an important bearing on the physical properties of the final block copolymer.

4.2.1.2.4 Use Pattern

Few materials are as compatible with as many processing techniques or are used in as many commercial applications as polypropylene. It is found in everything from flexible and rigid packaging to fibers and large molded parts for automotive and consumer products. Largely conforming to this diversity of applications is the fact that the material can be processed by most methods, including extrusion, extrusion coating, blown and cast film, blow molding, injection molding, and thermoforming.

Polypropylene fibers and filaments form the largest market area, which is comprised of several segments with carpeting applications being the largest; these include primary and secondary woven and

nonwoven uses, carpet backing face yarns, indoor/outdoor constructions, automotive interior mats and trunk linings, and synthetic turf.

The good wickability of PP is utilized in such nonwoven applications as disposable diaper. Other applications include clothing inner liners, drapes and gowns, sleeping bags, wall coverings, wiping cloths, and tea bags. Furniture and automotive upholstery fabrics are produced from both continuous monofilament and staple fibers.

The second largest PP market is film, both oriented (OPP) and cast. Large users of OPP films are packaging for snack foods, bakery products, dry foods, candy, gum, cheese, tobacco products, and electrical capacitors. Cast (unoriented) film is used for packaging textile soft goods, cheese, snack foods, and bakery products.

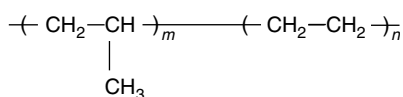
Largest users of injection molded PP are in transportation, particularly automotive and truck batter cases. PP copolymers have secured about 90% of this market as a result of a drive by automotive manufacturers to reduce weight and cost. In addition to being lightweight, PP also provides outstanding resistance to creep and fatigue, high temperature rigidity, impact strength, and resistance to corrosion.

The next largest molded product market for PP is packaging, especially closures and containers. Child-resistant, tamperproof, linerless features are important design factors as also inherent chemical resistance, stress-crack resistance, and high productivity at low cost. Housewares utilize random copolymers for refrigerator and shelf-storage containers and lids. Medium-impact copolymers are used for hot/cold thermos containers, lunch boxes, coolers, and picnic ware.

Medical applications of PP such as disposable syringes, hospital trays, and labware are contingent on sterilizability, either autoclaving or radiation. Disposable syringes that are sterilized by radiation require special formulations to prevent discoloration (yellowing) or brittleness as a consequence of degradation and cross-linking.

PP finds highly successful uses in both major and small appliances. Washing machines, dish washers, tub liners, agitators, bleach and detergent dispensing units, valve and control assemblies, drain tubes, pump housings, door liners, coffee makers, hair dryers, vacuum cleaners, can openers, knife sharpeners, room humidifiers and dehumidifiers, floor and ceiling fans, and window air-conditioner units are some examples.

4.2.1.3 Polyallomer



A proprietary polymerization process, developed in the mid 1960s by staff researchers of Eastman Chemical Products, produces copolymers of 1-olefins that give a degree of crystallinity normally obtained only with homopolymers. The term polyallomer was coined to identify the polymers manufactured by this process and to distinguish them from conventional copolymers. The polyallomer materials available today are based on block copolymers of propylene and ethylene.

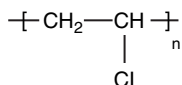
Polyallomers combine the most desirable properties of both crystalline polypropylene and high-density polyethylene (HDPE) and can offer impact strengths three or four times that of polypropylene. Resistance to heat distortion is better than that of HDPE but not quite as good as that of polypropylene. Polyallomer has better abrasion resistance than polypropylene and comparable hinge-forming characteristics.

Polyallomer lightweight cases can be molded entirely in one piece. Back, front, hinges, handles, and snap clasps can be molded in at the same time in a wide range of colors. Polyallomer is thus used in such injection molded items as fishing tackle boxes, typewriter cases, gas-mask cases, and bowling-ball bags.

Shoe toes molded of polyallomer resist cracking and denting under repeated hammer blows. They withstand temperatures from -40°C to 150°C and can withstand up to 300 pounds of force (1335 N).

Polyallomers can be processed easily on conventional molding and extruding equipment. Polypropylene color concentrates can be used to color polyallomer, since these two polymers are compatible.

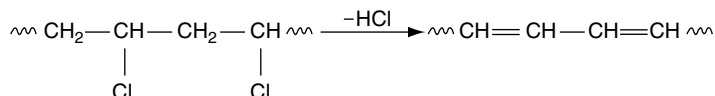
4.2.1.4 Poly(Vinyl Chloride)



Monomer	Polymerization	Major Uses
Vinyl chloride	Free-radical-initiated chain polymerization	Pipe and fittings (35%), film and sheet (15%), flooring materials (10%), wire and cable insulation (5%), automotive parts (5%), adhesives and coatings (5%)

PVC is produced by polymerization of vinyl chloride by free-radical mechanisms, mainly in suspension and emulsion, but bulk and solution processes are also employed to some extent [11–14]. (The control of vinyl chloride monomer escaping into the atmosphere in the PVC production plant has become important because cases of angiosarcoma, a rare type of liver cancer, were found among workers exposed to the monomer. This led to setting of stringent standards by governments and modification of manufacturing processes by the producers to comply with the standards.)

At processing temperatures used in practice (150–200°C), sufficient degradation may take place to render the product useless. Evidence points to the fact that dehydrochlorination occurs at an early stage in the degradation process and produces polyene structures:



It is believed that the liberated hydrogen chloride can accelerate further decomposition and that oxygen also has an effect on the reaction. However, incorporation of certain materials known as *stabilizers* retards or moderates the degradation reaction so that useful processed materials can be obtained. Many stabilizers are also useful in improving the resistance of PVC to weathering, particularly against degradation by UV radiation.

4.2.1.4.1 Characterization of Commercial Resins

Commercial PVC polymers are largely amorphous with molecular weights in the range $\bar{M}_w = 100,000$ –200,000 and $\bar{M}_n = 45,000$ –64,000, although values may be as low as 40,000 and as high as 480,000 for \bar{M}_w . In practice, the ISO viscosity number is often used to characterize the molecular weight of a PVC polymer. Table 4.2 compares typical correlations between number and weight average molecular weights with ISO numbers. Most general purpose polymer for use in plasticized PVC compounds have ISO numbers of about 125. Because of processing problems the polymer used for unplasticized PVC compounds have lower molecules weights, typical ISO numbers being 105 for pipe, 85–95 for rigid sheet, and as low as 70 for injection molding compounds [14].

With commercial polymers the major differences are in the characteristics of the particle, i.e., its shape, size, size distribution, and porosity. Such differences considerably affect the processing behavior of a polymer.

Considerable effort has been expended to develop suitable process to control porosity, surface area, and diffusivity of PVC particles and this has led to great improvements over the years in the processability of PVC.

TABLE 4.2 Molecular Weight Characterization of PVC

Average Molecular Weight		ISO/R174-1961(E): Viscosity Number
Weight	Number	
54,000	26,000	57
70,000	36,000	70
1,00,000	45,500	87
1,40,000	55,000	105
2,00,000	64,000	125
2,60,000	73,000	145
3,40,000	82,000	165

Source: Matthews, G. A. R. 1972. Vinyl and Allied Polymers, Vol. 1. *Vinyl Chloride and Vinyl Acetate Polymers*, Iliffe, London, UK.

If PVC polymer particles are mixed, at room temperature, with plasticizers, the immediate product may take one of two forms. If the plasticizer quantity is insufficient to fill all the gaps between the particles, a mush will be produced. If all the voids are filled then the particles will become suspended in the excess plasticizer and a paste will be formed.

The viscosity of a PVC paste (see Plastisol Casting in [Chapter 2](#)) made from a fixed polymer–plasticizer ratio depends to a great extent on the particle size and size distribution. To obtain a low viscosity paste the amount of plasticizer required to fill the voids between particles should be low so that more plasticizer is available to act as a lubricant for the particles, facilitating their general mobility in suspension. Thus in general PVC pastes in which the polymer has a wide particle-size distribution (but within limits set by problems of significant plasticizer absorption even at room temperature by very small particles and settling caused by large particles) so that particles pack efficiently and leave less voids (see [Figure 4.5a](#)) will have lower viscosity than those of constant particle size ([Figure 4.5b](#)).

The use of “filler” polymers in increasing quantities in PVC paste technology is an extension of this principle. These filler polymers are made by suspension (granular, dispersion) polymerization and by themselves the particles are too large to make stable pastes. However, in the presence of much smaller paste polymer particles they remain in stable suspension. As shown in [Figure 4.6](#), the replacement in space of a mixture of paste-polymer particles and plasticizer by a large granular polymer particle releases plasticizer which then acts as a lubricant, i.e., a viscosity depressant.

PVC pastes exhibit complex rheological behavior with the viscosities showing dependence on the shear rate and on the time of shear. A paste viscosity may increase with shear rate (*dilatancy*) or decrease (*shear thinning* or *pseudoplasticity*). Some pastes may show dilatant tendencies over one range of shear rates but

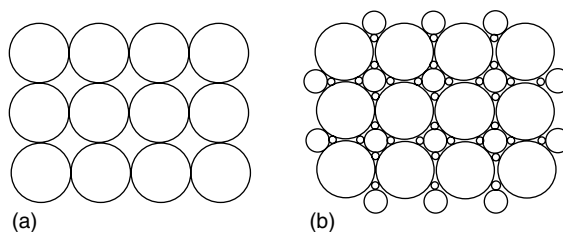


FIGURE 4.5 (a) PVC paste polymer particles with homogeneous particle size—less efficient packing. (b) PVC paste polymer particles with distribution of size—efficient packing. (After Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.)

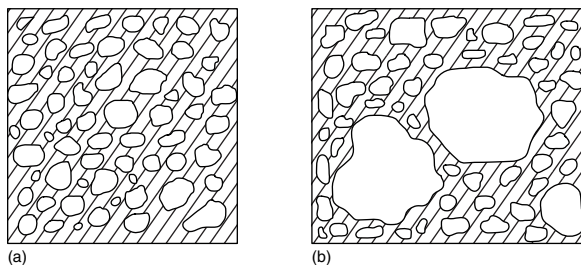


FIGURE 4.6 (a) PVC paste polymer suspended in plasticizer. (b) PVC paste containing filler polymer. Less plasticizer is required to fill voids in unit volume. (After Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.)

be shear thinning over another range. The viscosities may also decrease with time of stirring (*thixotropy*) or increase with it (*rheopexy*) [14].

It has been observed that spherical particles with distribution of size giving a high degree of packing are closest to Newtonian liquids in their behavior. Spherical particles of homogeneous size, however, give shear thinning pastes. This may be due to the fact that these particles tend to aggregate at rest while shearing causes disaggregation and hence easier movement of particles. Very coarse and lumpy uneven granules do not slide past each other in pastes and tend to become more entangled as shear rate increases. Such pastes commonly show dilatant behavior.

4.2.1.4.2 *Compounding Ingredients*

PVC is a colorless rigid material with limited heat stability and with a tendency to adhere to metallic surfaces when heated. For these and other reasons it is necessary to compound the polymer with other ingredients to make useful products. It is possible in this way to make a wide range of products including rigid piping and soft elastic cellular materials.

A PVC compound may contain, besides the polymer, the following ingredients: stabilizers, plasticizers, extenders, lubricants, fillers, pigments, and polymeric processing aids. Other ingredients also used occasionally include impact modifiers, fire retardants, optical bleaches, and blowing agents.

4.2.1.4.3 *Stabilizers*

The most important class of stabilizers are the lead compounds which form lead chloride on reaction with the hydrogen chloride evolved during decomposition. Basic lead carbonate (white lead), which has a low weight cost, is more commonly used. A disadvantage of lead carbonate is that it may decompose with the evolution of carbon dioxide at higher processing temperatures and lead to a porous product. For this reason, tribasic lead sulfate, which gives PVC products with better electrical insulation properties than lead carbonate, is often used despite its somewhat higher weight cost.

Other lead stabilizers are of much more specific applications. For example, dibasic lead phthalate, which is an excellent heat stabilizer, is used in heat-resistant insulation compounds (e.g., in 150°C wire), in high-fidelity gramophone records, in PVC coatings for steel, and in expanded PVC formulation.

The use of lead compounds as stabilizers has been subjected to regulation because of its toxicity. Generally, lead stabilizers are not allowed in food-packaging PVC materials, but in most countries they are allowed in PVC pipes for conveying drinking water, with reduction in the level of use of such stabilizers.

Today the compounds of cadmium, barium, calcium, and zinc have gained prominence as PVC stabilizers. A modern stabilizing system may contain a large number of components. A typical cadmium–barium packaged stabilizer may have the following composition: cadmium–barium phenate 2–3 parts, epoxidized oils 3–5 parts, trisnonyl phenyl phosphite 1 part, stearic acid 0.5–1 part, and zinc octoate 0.5 part by weight. For flooring compositions, calcium–barium, magnesium–barium, and copper–barium

compounds are sometimes used in conjunction with pentaerythritol (which has the function of reducing color by chelating iron present in asbestos).

Another group of stabilizers are the organotin compounds. Development of materials with low toxicity, excellent stabilizing performance, and improving relative price situation has led to considerable growth in the organotin market during the last decade. Though the level of toxicity of butyltins is not sufficiently low for application in contact with foodstuffs, many of the octyltins, such as dioctyltin dilaurate and dioctyltin octylthioglycolate, meet stringent requirements for use in contact with foodstuffs. Further additions to the class of organotins include the estertins characterized by low toxicity, odor, and volatility, and the methyltins having higher efficiency per unit weight compared with the more common organotins.

Organotin compounds that are salts of alkyltin oxides with carboxylic acids (e.g., dioctyltin dilaurate) are usually called organotin carboxylates. Organotin compounds with at least one tin-sulfur bond (e.g., dioctyltin octylthioglycolates) are generally called organotin mercaptides. The latter are considered to be the most efficient and most universal heat stabilizers. The important products which are on the market have the following structures:



Where R_1 is $\text{H}_3\text{C}-$, $n\text{-C}_4\text{H}_9-$, $n\text{-C}_8\text{H}_{17}-$, $n\text{-C}_{12}\text{H}_{25}-$ or $\text{alkyl-O-CO-CH}_2\text{-CH}_2-$, and R_2 is $-\text{CH}_2\text{-CO-O-alkyl}$, $-\text{CH}_2\text{-CH}_2\text{-CO-O-alkyl}$, $-\text{CH}_2\text{-CH}_2\text{-O-CO-alkyl}$ or $-\text{alkyl}$.

One of the most important properties—not only of the sulfur-containing tin stabilizers but also of the whole group of organotin stabilizers—is absolute crystal clarity, which can be achieved by means of a proper formulation. Clarity is required for bottles, containers, all kinds of packaging films, corrugated sheets, light panels, and also for hose, profiles, swinging doors, and transparent top coats of floor or wall coverings made from plasticized PVC.

4.2.1.4.4 Plasticizers

In addition to resin and stabilizers, a PVC compounds may contain ingredients such as plasticizers, extenders, lubricants, fillers, pigments, polymeric processing aids, and impact modifiers.

Plasticizers (see also [Chapter 1](#)) are essentially nonvolatile solvents for PVC. At the processing temperature of about 150°C , molecular mixing occurs in a short period of time to give products of greater flexibility. Phthalates prepared from alcohols with about eight carbon atoms are by far the most important class and constitute more than 70% of plasticizers used. For economic reasons, diisooctyl phthalate (DIOP), di-2-ethylhexyl phthalate (DEHP or DOP), and the phthalate ester of the C7-C9 oxoalcohol, often known as dialphanyl phthalate (DAP) because of the ICI trade name “Alphanol-79” for the C7-C9 alcohols, are used. DIOP has somewhat less odor, whereas DAP has the greatest heat stability. Dibutyl phthalate and diisobutyl phthalate are also efficient plasticizers and continue to be used in PVC (except in thin sheets) despite their high volatility and water extractability.

Phosphate plasticizers such as tritoly phosphate and trixylyl phosphate are generally used where good flame resistance is required, such as in insulation and mine belting. These materials, however, are toxic and give products with poor low-temperature resistance, i.e., with a high cold flex temperature (typically, -5°C).

For applications where it is important to have a compound with good low-temperature resistance, aliphatic ester plasticizers are of great value. Dibutyl sebacate, dioctyl sebacate, and, more commonly, cheaper esters of similar effect derived from mixed acids produced by the petrochemical industry are used. These plasticizers give PVC products with a cold flex temperature of -42°C .

Esters based on allyl alcohol, such as diallyl phthalate and various polyunsaturated acrylates, have proved useful in improving adhesion of PVC to metal. They may be considered as polymerizable plasticizers. In PVC pastes they can be made to cross-link by the action of peroxides or perbenzoates

when the paste is spread on to metal, giving a cured coating with a high degree of adhesion [14]. The high adhesion of these rather complex compounds has led to their development as metal-to-metal adhesives used, for example, in car manufacture. Metal coatings may also be provided from plasticized powders containing polymerizable plasticizers by means of fluidized bed or electrostatic spraying techniques.

4.2.1.4.5 Extenders

In the formulation of PVC compounds it is not uncommon to replace some of the plasticizer with an extender, a material that is not in itself a plasticizer because of its very low compatibility but that can be used in conjunction with a true plasticizer. Commercial extenders are cheaper than plasticizers and can often be used to replace up to one-third of the plasticizer without seriously affecting the properties of the compound. Three commonly employed types of extenders are chlorinated paraffin waxes, chlorinated liquid paraffinic fractions, and oil extracts [14].

4.2.1.4.6 Lubricants

In plasticized PVC it is common practice to incorporate a lubricant whose main function is to prevent sticking of the compound to processing equipment [14]. The material used should have limited compatibility such that it will sweat out during processing to form a film between the bulk of the compound and the metal surfaces of the processing equipment. The additives used for such a purpose are known as *external lubricants*.

In the United States normal lead stearate is commonly used. This material melts during processing and lubricates like wax. Also used is dibasic lead stearate, which does not melt but lubricates like graphite and improves flow properties. In Britain, stearic acid is mostly used with transparent products, calcium stearate with nontransparent products.

An unplasticized PVC formulation usually contains at least one other lubricant, which is mainly intended to improve the flow of the melt, i.e., to reduce the apparent melt viscosity. Such materials are known as *internal lubricants*. Unlike external lubricants they are reasonably compatible with the polymer and are more like plasticizers in their behavior at processing temperatures, whereas at room temperature this effect is negligible. Among materials usually classified as internal lubricants are montan wax derivatives, glyceryl monostearate, and long-chain esters such as cetyl palmitate.

4.2.1.4.7 Fillers

Fillers are commonly employed in opaque PVC compounds to reduce cost and to improve electrical insulation properties, to improve heat deformation resistance of cables, to increase the hardness of a flooring compound, and to reduce tackiness of highly plasticized compounds. Various calcium carbonates (such as whiting, ground limestone, precipitated calcium carbonate) are used for general-purpose work, china clay is commonly employed for electrical insulation, and asbestos for flooring applications. Also employed occasionally are the silicas and silicates, talc, light magnesium carbonate, and barytes (barium sulfate).

4.2.1.4.8 Pigments

Many pigments are now available commercially for use with PVC. Pigment selection should be based on the pigments ability to withstand process conditions, its effect on stabilizer and lubricant, and its effect on end-use properties, such as electrical insulation.

4.2.1.4.9 Impact Modifiers and Processing Aids

Unplasticized PVC present some processing difficulties due to its high melt viscosity; in addition, the finished product is too brittle for some applications. To overcome these problems and to produce toughening, certain polymeric additives are usually added to the PVC. These materials, known as *impact modifiers*, are generally semicompatible and often somewhat rubbery in nature [14]. Among the most important impact modifiers in use today are butadiene–acrylonitrile copolymers (nitrile rubber), acrylonitrile–butadiene–styrene (ABS) graft terpolymers, methacrylate–butadiene–styrene (MBS) terpolymers, chlorinated polyethylene, and some polyacrylates.

ABS materials are widely used as impact modifiers, but they cause opacity and have only moderate aging characteristics. Many grades also show severe *stress whitening*. A phenomenon advantageously employed in labeling tapes, such as Dymotape. MBS modifiers have been used such as where tough PVC materials of high clarity are desired (e.g., bottles and film). Chlorinated polyethylene has been widely used as an impact modifier where good aging properties are required.

A number of polymeric additives are also added to PVC as *processing aids*. They are more compatible with PVC and are included mainly to ensure more uniform flow and thus improve the surface finish. In chemical constitution they are similar to impact modifiers and include ABS, MBS, acrylate–methacrylate copolymers, and chlorinated polyethylene.

Typical formulations of several PVC compounds for different applications are given in [Appendix A11](#).

4.2.1.4.10 Properties and Applications

PVC is one of the most versatile of plastics and its usage ranges widely from building construction to toys and footwear. PVC compounds are made in a wide range of formulations, which makes it difficult to make generalizations about their properties. Mechanical properties are considerably affected by the type and amount of plasticizer. Table 4.3 illustrates differences in some properties of three distinct types of compound. To a lesser extent, fillers also affect the physical properties.

Unplasticized PVC (UPVC) is a rigid material, whereas the plasticized material is tough, flexible, and even rubbery at high plasticizer loadings. Relatively high plasticizer loadings are necessary to achieve many significant improvement in impact strength. Thus incorporation of less than 20% plasticizer does not give compounds with impact strength higher than that of unplasticized grades. Lightly plasticized grades are therefore used when the ease of processing is more important than achieving good impact strength.

PVC is resistant to most aqueous solutions, including those of alkalis and dilute mineral acids. The polymer also has a good resistance to hydrocarbons. The only effective solvents appear to be those which are capable of some form of interaction with the polymer. These include cyclohexanone and tetrahydrofuran.

At ordinary temperatures, PVC compounds are reasonably good electrical insulators over a wide range of frequencies, but above the glass transition temperature their value as an insulator is limited to low-frequency applications. The volume resistivity decreases as the amount of plasticizer increases.

PVC has the advantage over other thermoplastic polyolefins of built-in fire retardancy because of its 57% chlorine content.

Copolymers of vinyl chloride with vinyl acetate have lower softening points, easier processing, and better vacuum-forming characteristics than the homopolymers. They are soluble in ketones, esters, and certain chlorinated hydrocarbons, and have generally inferior long-term heat stability.

About 90% of the PVC produced is used in the form of homopolymers, the other 10% as copolymers and terpolymers. The largest application of homopolymers PVC compounds, particularly unplasticized grades, is for rigid pipes and fittings, most commonly as suspension homopolymers of high bulk density compounded as *powder blends*.

TABLE 4.3 Properties of Three Types of PVC Compounds

Property	Unplasticized PVC	PVC + DIOP (50 Parts Per 100 Resin)	Vinyl Chloride–Vinyl Acetate Copolymer (Sheet)
Specific gravity	1.4	1.31	1.35
Tensile strength lbf/in. ²	8500	2700	7000
MPa	58	19	48
Elongation at break (%)	5	300	5
Vicat softening (°C)	80	Flexible at room temperature	70

Source: Bryctson, J. A. 1982. *Plastics Materials*, Butterworth Scientific, London, UK.

In addition to the afore said properties, UPVC has an excellent resistance to weathering. Moreover, when the cost of installation is taken into account, the material frequently turns out to be cheaper. UPVC is therefore becoming used increasingly in place of traditional materials. Important uses include translucent roof sheathing with good flame-retarding properties, window frames, and piping that neither corrodes nor rots.

As a pipe material PVC is widely used in soil pipes and for drainage and above-ground applications. Piping with diameters of up to 60 cm is not uncommon.

UPVC is now being increasingly used as a wood replacement due to its more favorable economics, taking into account both initial cost and installation. Specific applications include bench-type seating at sports stadia, window fittings, wall-cladding, and fencing. UPVC bottles have better clarity, oil resistance, and barrier properties than those made from polyethylene. Compared with glass they are also lighter, less brittle, and possess greater design flexibility. These products have thus made extensive penetration into the packaging market for fruit juices and beverages, as well as bathroom toiletry. Sacks made entirely of PVC enable fertilizers and other products to be stored outdoors.

The largest applications of plasticized PVC are wire and cable insulation and as film and sheet. PVC is of great value as an insulator for direct-current and low-frequency alternating-current carriers. It has almost completely replaced rubber in wire insulation. PVC is widely used in cable sheathing where polyethylene is employed as the insulator.

Other major outlets of plasticized PVC include floor coverings, leathercloth, tubes and profiles, injection moldings, laminates, and paste processes.

When a thin layer of plasticized PVC is laminated to a metal sheet, the bond may be strong enough that the laminate can be punched, cut, or shaped without parting the two layers. A pattern may be printed or embossed on the plastic before such fabrication. Typewriter cases and appliance cabinets have been produced with such materials.

PVC leathercloth has been widely used for many years in upholstery and trim in car applications, house furnishings, and personal apparel. The large-scale replacement of leather by PVC initiated in the 1950s and 1960s was primarily due to the greater abrasion resistance, flex resistance, and washability of PVC. Ladies handbags are frequently made from PVC leathercloth. House furnishing applications include kitchen upholstery, printed sheets, and bathroom curtains. Washable wallpapers are obtained by treating paper with PVC compounds.

Special grades of PVC are used in metal-finishing applications, for example, in stacking chairs. Calendered plasticized PVC sheet is used in making plastic rainwear and baby pants by the high-frequency welding technique. The application of PVC in mine belting is still important in terms of the actual tonnage of material consumption. All-PVC shoes are useful as beachwear and standard footwear. PVC has also proved to be an excellent abrasion-resistant material for shoe soles. PVC adhesives, generally containing a polymerizable plasticizer, are useful in many industries.

The two main applications of vinyl chloride–vinyl acetate copolymers are phonograph records and vinyl floor tiles. The copolymers contain an average of about 13% of vinyl acetate. They may be processed at lower temperatures than those used for the homopolymers. Phonograph records contain only a stabilizer, lubricant, pigment, and, possibly, an antistatic agent; there are no fillers. Preformed resin biscuits are normally molded in compression presses at about 130–140°C. The press is a flash mold that resembles a waffle iron. The faces of the mold may be nickel negatives of an original disc recording that have been made by electrodeposition.

Floor tiles contain about 30–40 parts plasticizer per 100 parts copolymer and about 400 parts filler (usually a mixture of asbestos and chalk). Processing involves mixing in an internal mixer at about 130°C, followed by calendaring at 110–120°C.

4.2.1.4.11 Pastes

A PVC paste is obtained when the voids between the polymer particles in a powder are completely filled with plasticizer so that the particles are suspended in it. To ensure a stable paste, there is an upper limit and a lower limit to the order of particle size. PVC paste polymers have an average particle size of about

TABLE 4.4 Typical Formulations^a of Three Types of PVC Pastes

Ingredient	Plastisol	Organosol	Plastigel
PVC paste polymer	100	100	100
Plasticizer (e.g., DOP)	80	30	80
Filler (e.g., china clay)	10	10	10
Stabilizer (e.g., white lead)	4	4	4
Naphtha	—	50	—
Aluminum stearate	—	—	4

^a Parts by weight.

0.2–1.5 μm . The distribution of particle sizes also has significant influences on the flow and fluxing characteristics of the paste.

The main types of PVC pastes are plastisols, organosols, plastisols incorporating filler polymers (including the rigisols), plastigels, hot-melt compounds, and compounds for producing cellular products. Typical formulations of the first three types are shown in Table 4.4. The processing methods were described in Chapter 2.

Plastisols are of considerable importance commercially. They are converted into tough, rubbery products by heating at about 160°C (*gelation*). *Organosols* are characterized by the presence of a volatile organic diluent whose sole function is to reduce the paste viscosity. The diluent is removed after application and before gelling the paste.

Another method of reducing paste viscosity is to use a *filler polymer* to replace a part of the PVC paste polymer. The filler polymer particles are too large to make stable pastes by themselves, but in the presence of paste-polymer particles they remain in stable suspension. Being very much larger than paste-polymer particles and having a low plasticizer absorption, the take up large volumes in the paste and make more plasticizer available for particle lubrication, thus reducing paste viscosity. The use of filler polymers has increased considerably in recent years. Pastes prepared using filler polymers and only small quantities of plasticizer (approximately 20 parts per 100 parts of polymer) are termed *rigisols*.

The incorporation of such materials as aluminum stearate, fumed silicas, or certain bentonites gives a paste that shows pronounced Bingham Body behavior (i.e., it only flows on application of shearing stress above a certain value). Such putty-like materials (called *pastigels*), which are usually thixotropic may be hand-shaped and subsequently gelled (see ‘Plastisol Casting’ in Chapter 2).

Plastigels are often compared with *hot-melt PVC compounds*. These later materials are prepared by fluxing polymer with large quantities of plasticizers and extenders. They melt at elevated temperatures and become very fluid, so they may be poured. These compounds are extensively used for casting and prototype work.

Sigma-blade trough mixers are most commonly used for mixing PVC pastes. It is common practice to mix the dry ingredients initially with part of the plasticizer so that the shearing stresses are high enough to break down the aggregates. The remainder of the plasticizer is then added to dilute the product. The mix is preferably deaerated to remove air bubbles before final processing.

A large proportion of PVC paste is used in the manufacture of leathercloth by a *spreading technique*. A layer of paste is smeared on the cloth by drawing the latter between a roller or endless belt and a doctor blade against which there is a rolling bank of paste. The paste is gelled by passing through a heated tunnel or under infrared heaters. Embossing operations may be carried out by using patterned rollers when the gelled paste is still hot. The leathercloth is then cooled and wound up. Where it is desired that the paste should enter the interstices of the cloth, a shear-thinning (pseudo-plastic) paste is employed. Conversely, where strike-through should be minimized, a dilatant paste (viscosity increases with shear rate) is employed.

Numerous methods exist for producing cellular products (see Chapter 2) from PVC pastes. Closed-cell products can be made if a blowing agent such as azodiisobutyronitrile is incorporated into the paste.

The paste is then heated in a mold to cause the blowing agent to decompose and the compound to gel. Since the mold is full, expansion does not take place at this stage. The unexpanded block is removed after thoroughly cooling the mold and is heated in an oven at about 100°C to produce uniform expansion.

One method of producing a flexible, substantially open-cell product is to blend the paste with carbon dioxide (either as dry ice or under pressure). The mixture is heated to volatilize the carbon dioxide to produce a foam, which is then gelled at a higher temperature.

4.2.1.4.12 Chlorinated PVC

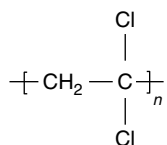
Closely related to PVC, but with distinct properties of its own, is chlorinated poly(vinyl chloride) (CPVC), a polymer produced by postchlorination of PVC. The effect of adding more chlorine to the PVC molecule is to raise the T_g of the base resin to 115–135°C (239–275°F) range and the heat deflection temperature under load to around 115°C (239°F). CPVC also has higher tensile strength, higher modulus, and greater resistance to combustion and smoke generation.

The compounding process for CPVC is similar to that used in PVC compounding, but is more complex. Processing of CPVC is done by the traditional thermoplastic operations of extrusion, calendaring, and injection molding. However, because of the high temperature of CPVC polymer melt (205–230°C), extrusion of the resin requires chrome-plated or stainless steel dies. Injection molding of CPVC requires low-compression screws with good exit depth and molds should be stainless steel or chrome- or nickel-plated.

Traditional applications of CPVC compounds are hot and cold water distribution piping, fittings, and valves that can handle industrial liquids and chemicals. The increasing popularity of CPVC in its application in hot and cold water pipes in residential units stems from its continuous-use rating of 80°C (176°F) and 100 psi, its approval for potable water by the National Sanitation Foundation (U.S.A.), and its low heat loss along with lack of sweating and scale buildup.

The high-heat capability, low combustion ratings, and resistance to grease- and oil-induced cracking have made CPVC a strong contender for applications in automotive interiors. With its combination of excellent properties of PVC and the added ability to perform at elevated temperatures, CPVC is beginning to penetrate markets formerly dominated by metals or the more expensive engineering polymers.

4.2.1.5 Poly(Vinylidene Chloride)



Monomer	Polymerization	Major Uses
Vinylidene chloride	Free-radical-initiated chain polymerization	Film and sheeting for food packaging

The polymer may be prepared readily by free-radical mechanisms in bulk, emulsion, and suspension; the latter technique is usually preferred on an industrial scale. Copolymers of vinylidene chloride with vinyl chloride, acrylates, and acrylonitrile are also produced.

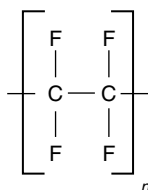
Since the poly(vinylidene chloride) molecule has an extremely regular structure (and the question of tacticity does not arise), the polymer is capable of crystallization. Because of the resultant close packaging and the presence of heavy chloride atoms the polymer has a high specific gravity (1.875) and a low permeability to vapors and gases. The chlorine present gives a self-extinguishing polymer. Vinylidene chloride–vinyl chloride copolymers are also self-extinguishing and possess very good resistance to a wide range of chemicals, including acids and alkalis. Because of a high degree of crystallization, even in the

copolymers, high strengths are attained even though the products have relatively low molecular weights ($\sim 20,000$ – $50,000$).

Both poly(vinylidene chloride) and copolymers containing vinylidene chloride are used to produce flexible films and coatings. Flexible films are used extensively for food packaging because of their superior barrier resistance to water and oxygen. The coating resins are used for cellophane, polyethylene, paper, fabric, and container liner applications. Dow's trade name for a copolymer of vinylidene chloride (87%) and vinyl chloride (13%) is *Saran*. Biaxially stretched Saran film is a useful, though expensive, packaging material possessing exceptional clarity, brilliance, toughness, and impermeability to water and gases.

Vinylidene chloride–vinyl chloride copolymers are used in the manufacture of filaments. The filaments have high toughness, flexibility, durability, and chemical resistance. They find use in car upholstery, deck-chair fabrics, decorative radio grilles, doll hair, filter presses, and other applications. A flame-resisting fiber said to be a 50:50 vinylidene chloride–acrylonitrile copolymer is marketed by Courtaulds with the name Teklan.

4.2.1.6 Polytetrafluoroethylene and Other Fluoropolymers



Monomer	Polymerization	Major Uses
Tetrafluoroethylene, hexafluoropropylene, chlorotrifluoroethylene, vinyl fluoride, vinylidene fluoride, perfluoroalkyl vinyl ether	Free-radical-initiated chain polymerization	Coatings for chemical process equipment, cable insulation, electrical components, nonsticking surfaces for cookware

Polytetrafluoroethylene (PTFE) was discovered in 1947. Today PTFE probably accounts for at least 85% of the fluorinated polymers and, in spite of its high cost, has a great diversity of applications [16–18]. It is produced by the free-radical chain polymerization of tetrafluoroethylene.

With a linear molecular structure of repeating $-\text{CF}_2-\text{CF}_2-$ units, PTFE is a highly crystalline polymer with a melting point of 327°C . Density is 2.13 – 2.19 g/cm^3 .

Commercially PTFE is made by two major processes—one leading to the so-called granular polymer, the second to a dispersion of polymers of much finer particle size and lower molecular weight.

Since the carbon–fluorine bond is very stable and since the only other bond present in PTFE is the stable C–C bond, the polymer has a high stability, even when heated above its melting point. Its upper-use temperature is given as 260°C . It is reported to give ductile rather than brittle failures at temperatures just above absolute zero, signifying a useful temperature range of more than 500°C . In many instances PTFE has been used satisfactorily as a totally enclosed gasket for considerable periods of time at temperatures well above the recommended upper-use temperature.

Because of its high crystallinity ($> 90\%$) and incapability of specific interaction, PTFE has exceptional chemical resistance and is *insoluble in all organic solvents*. (PTFE dissolves in certain fluorinated liquids such as perfluorinated kerosenes at temperatures approaching the melting point of the polymer.) At room temperature it is attacked only by alkali metals and, in some cases, by fluorine. Treatment with a solution of sodium metal in liquid ammonia sufficiently alters the surface of a PTFE sample to enable it to be cemented to other materials by using epoxide resin adhesives.

PTFE has good weathering resistance. The polymer is not wetted by water and has negligible water absorption (0.005%). The permeability of gases is low—the rate of transmission of water vapor is approximately half that of poly(ethylene terephthalate) and low-density polyethylene. PTFE is however degraded by high-energy radiation. For example, the tensile strength of a given sample may be halved by exposure to a dosage of 70 Mrad.

PTFE is a tough, flexible material of moderate tensile strength (2500–3800 psi, i.e., 17–21 MPa) at 23°C. Temperature has a considerable effect on its properties. It remains ductile in compression at temperatures as low as 4 K (−269°C). The creep resistance is low in comparison to other engineering plastics. Thus, even at 20°C unfilled PTFE has a measurable creep with compression loads as low as 300 psi (2.1 MPa).

The coefficient of friction is unusually low and is lower than almost any other material. The values reported in the literature are usually in the range 0.02–0.10 for polymer to polymer and 0.09–0.12 for polymer to metal. The polymer has a high oxygen index and will not support combustion.

PTFE has outstanding insulation properties over a wide range of temperatures and frequencies. The volume resistivity exceeds 10^{20} ohm-m. The power factor (<0.003 at 60 Hz and <0.0003 at 10^6 Hz) is negligible in the temperature range −60°C to +250°C. PTFEs low dielectric constant (2.1) is unaffected by frequency. The dielectric strength of the polymer is 16–20 kV/mm (short time on 2-mm thick sheet).

4.2.1.6.1 Processing

PTFE is commonly available in three forms [14] (a) granular polymers with average particle size of 300–600 μm ; (b) dispersion polymers (obtained by coagulation of a dispersion) consisting of agglomerates with an average diameter of 450 μm , which are made up of primary particles 0.1 μm in diameter; and (c) dispersion (lattices) containing about 60% polymer in the form of particles with an average diameter of about 0.16 μm .

ASTM Standard Specification D1457 covers the forms sold as powders and defines seven type of PTFE molding and extrusion materials ranging from general-purpose granular resin (Type I) to presintered resin (Type VII). ASTM D4441 describes eight types of aqueous dispersion that differ, primarily, in the solids content and the amount of surfactant.

PTFE cannot be processed by the usual thermoplastics processing techniques because of its exceptionally high melt viscosity ($\sim 10^{10}$ – 10^{11} P at 350°C). Granular polymers are processed by press and sinter methods used in powder metallurgy. In principle, these methods involve performing the sieved powder by compressing in a mold at 1.0–3.5 tonf/in.² (16–54 MPa) usually at room temperature or at 100°C, followed by sintering at a temperature above the melting point (typically at about 370°C), and then cooling.

Free-sintering of the perform in an oven at about 380°C is also satisfactory. The sintering period depends on the thickness of the sample. For example, a 0.5-in. (1.25-cm)-thick sample will need sintering for 3.5 h. Granular polymers may also be extruded, though at very low rates (2.5–16 cm/min), by screw and ram extruders. The extrudates are reasonably free of voids.

Billets in sizes varying from less than a kilogram up 700 kg (among the largest moldings made of any plastic material) are made by perform sintering. The powder is placed in a mold at or slightly above room temperature and compressed at pressures from 2000–5000 psi (14–34 MPa). After being removed from the mold, the perform is sintered by heating it unconfined in an oven at temperatures in the range of 360–380°C for times ranging from a few hours to several days. The time-temperature schedule depends on the size and shape of the billet.

The billets are often in the form of cylinder, which are then mounted on a mandrel. Sheeting is prepared by skiving, much like plywood is cut from large logs. The sheeting is cut in the thickness range of 0.025 mm (0.001 in.) to 2.5 mm (0.1 in.).

With sheet molding, the procedures are very similar to those used as described above for billet molding except for the shape and size of the molding. This process is used for sheeting above 2.5 mm (0.1 in.) up to large blocks. The latter are used for a block method skiving operation similar to that used traditionally for cellulose nitrate.

With ram extrusion, the PTFE powder is fed into a cavity at one end of a heated tube. A reciprocating ram compacts the powder and forces in into the tube. While it is being transported down the length of the tube, the PTFE is melted and coalesced. Continuous lengths of sintered rod or shapes comes out of the other end of the extruder.

PTFE moldings and extrudates may be machined without difficulty. Continuous film may be obtained by peeling a pressure-sintered ring and welding it to a similar film by heat sealing under pressure at about 350°C.

A PTFE dispersion polymer leads to products with improved tensile strength and flex life. Preforms are made by mixing the polymer with 15–25% of a lubricant and extruded. This step is followed by lubricant removal and sintering. In a typical process a mixture of PTFE dispersion polymer (83 parts) and petroleum ether (17 parts) with a 100–120°C boiling range is compacted into a perform billet which is then extruded by a vertical ram extruder. The extrudate is heated in an oven at about 105°C to remove the lubricant and is then sintered at about 380°C. Because of the need to remove the lubricant, only thin sections can be produced by this process. Thin-walled tubes with excellent fatigue resistance can be produced, or wire can be coated with very thin coatings of PTFE.

Tapes also may be made by a similar process. However, in this case the lubricant used in a nonvolatile oil. The perform is extruded in the shape of a rod, which is then passed between a pair of calendared rolls at about 60–80°C. The unsintered tape finds an important application in pipe-thread sealing. If sintered tape is required, the calendared product is first degreased by passing through boiling trichloroethylene and then sintered by passing through a salt bath. The tape made in this way is superior to that obtained by machining granular polymer molding [14].

A convenient way to apply PTFE dispersions to surfaces is by use of aqueous dispersion coatings. For this a dispersion as provided by the manufacturer may be used. There are also many coating formulations that can be purchased for use in such applications as cookware and bakeware. Coating is done as dip coating and, with thickened dispersions, as roller coating.

The dispersion should have a concentration of 45–50% PTFE and 6–9% of a wetting agent, based on the amount of PTFE. Usually a nonionic agent is used, such as Triton X-100 from Rohm and Haas or similar materials from other suppliers. The amount of PTFE deposited on each coat must be restricted so as to prevent mud cracking when the coating is dried. For drying the coating, infrared lamps or forced-convection ovens at 85–95°C are usually used. Multiple coats are used to obtain thicker films.

Drying is followed by baking and sintering to remove the wetting agent and then coalesce the PTFE. Temperatures of 260–315°C are used for the baking and 360–400°C for the sintering. The time required for each of these steps varies from several seconds to a few minutes, depending on the shape of the surface and thickness of the coating. To obtain good homogeneity, multiple dips are used, with baking and sintering after each.

Casting is used to make thin films for use in such applications as heart–lung machines, special electronic equipment and various specialty applications. Often it is done by allowing the dispersion to flow onto a support surface, usually a polished stainless-steel belt, that carries the film through the successive steps of coating, drying, baking, sintering, recoating, and finally, stripping from the belt.

Glass-coated PTFE laminates may be produced by piling up layers of glass cloth impregnated with PTFE dispersions and pressing at about 330°C. Asbestos–PTFE laminates may be produced in a similar way. The dispersions can also be used for producing filled PTFE molding material. The process typically involves stirring fillers into the dispersion, coagulating with acetone, drying at 280–290°C, and disintegrating the resulting cake of material.

4.2.1.6.2 Applications

The exceptional properties of PTFE make it highly useful. It is selected for a wide range of applications that affect every person. The applications fall in the five areas that require one or more of its chemical, mechanical, electrical, thermal, and surface properties. In essentially every instance, a successful application employs at least two of the outstanding properties of this polymer. However, because of its high volume cost, PTFE is not generally used to produce large objects.

In many cases it is possible to coat a metal object with a layer of PTFE to meet the particular requirement. Nonstick home cookware is perhaps the best-known example. PTFE is used for lining chutes and coating other metal objects where low coefficients of friction, chemical inertness, nonadhesive characteristics are required. The same properties make PTFE useful for coverings on rollers in food processing equipment, xerographic copiers and saw blades, coatings on snow shovels, and many other similar applications. The Alaskan oil pipeline, for example, rests on PTFE-coated steel plates. Most new bridges and tunnels use similar supports.

Because of its exceptional chemical resistance over a wide temperature range, PTFE is used in a variety of seals, gaskets, packings, valve and pump parts, and laboratory equipment.

Its excellent electrical insulation properties and heat resistance lead to its use in high-temperature wire and cable insulation, molded electrical components, insulated transformers, hermetic seals for condensers, laminates for printed circuitry, and many other electrical applications.

Reinforced PTFE applications include bushings and seals in compressor hydraulic applications, automotive applications, and pipe liners. A variety of moldings are used in aircraft and missiles and also in other applications where use at elevated temperatures is required.

An important application for aqueous dispersions of PTFE is the architectural fabric market. This product consists of fiberglass fabric coated with special forms of the aqueous dispersion. The resulting material is used as roofs in a wide variety of buildings, especially where a large area must be covered with minimum support. Notable examples of such use are the Pontiac "Silver Dome," the airport terminal in Jeddah, Saudi Arabia (where 105 acres are enclosed), and many college and university stadiums or union buildings.

Copolymers of tetrafluoroethylene were developed in attempts to provide materials with the general properties of PTFE and the melt process-ability of the more conventional thermoplastics. Two such copolymers are tetrafluoroethylene-hexafluoropropylene (TFE-HFP) copolymers (Teflon FEP resins by Du Pont; FEP stands for fluorinated ethylene propylene) with a melting point of 290°C and tetrafluoroethylene-ethylene (ETFE) copolymers (Tefzel by Du Pont) with a melting point of 270°C. These products are melt processable. A number of other fluorine containing melt processable polymers have been introduced.

Polychlorotrifluoroethylene (PCTFE) was the first fluorinated polymer to be produced on an experimental scale and was used in the United States early in World War II. It was also used in the handling of corrosive materials, such as uranium hexafluoride, during the development of the atomic bomb.

PCTFE is a crystalline polymer with a melting point of 218°C and density of 2.13 g/cm³. The polymer is inert to most reactive chemicals at room temperature. However, above 100°C a few solvents dissolve the polymer, and a few, especially chlorinated types, swell it. The polymer is melt processable, but processing is difficult because of its high melt viscosity and its tendency to degrade, resulting in deterioration of its properties.

PCTFE is marketed by Hoechst as Hostaflon C2 and in the United States by Minnesota Mining and Manufacturing (3M) as Kel-F and by Allied Chemical as Halon. The film is sold by Allied Corp. as Aclar.

PCTFE is used in chemical processing equipment and cryogenic and electrical applications. Major applications include wafer boats, gaskets, O-rings, seals, and electrical components. PCTFE has outstanding barrier properties to gases, the PCTFE film has the lowest water-vapor transmission of any transparent plastic film. It is used in pharmaceutical packaging and other applications for its vapor barrier properties, including electroluminescent lamps.

Other melt-processable fluoroplastics include ethylene-chlorotrifluoroethylene (ECTFE) copolymer (melting point 240°C), polyvinylidene fluoride (PVDF) (melting point 170°C), and polyvinyl fluoride (PVF), which is commercially available only as film.

PVF is tough and flexible, has good abrasion and staining resistance, and has outstanding weathering resistance. It maintains useful properties over a temperature range of -70°C to 110°C. PVF can be laminated to plywood, hardboard, vinyl, reinforced polyesters, metal foils, and galvanized steel. These laminates are used in aircraft interior panels, lighting panels, wall coverings, and a variety of building

applications. PVF is also used as glazing in solar energy collectors. PVF film is marketed by Du Pont as Tedlar.

PVDF is correctly named poly(1,1-difluoroethylene) and represented by $(-\text{CF}_2\text{CH}_2-)_n$. It is a hard, tough thermoplastic fluoropolymer. PVDF is prepared by free-radical initiated polymerization, either in suspension or (usually) in emulsion systems. The basic raw material for PVDF is vinylidene fluoride ($\text{CH}_2=\text{CF}_2$), a preferred synthesis of which is dehydrochlorination of chlorodifluoroethane.

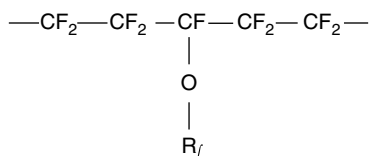
PVDF has the lowest melting point of any of the commercial fluoropolymers. As a result, its upper use temperature is limited to about 150°C , compared to values of 200°C for FEP and 260°C for PTFE. At temperatures in its useful range, however, PVDF maintains its stiffness and toughness very well.

PVDF exhibits the excellent resistance to harsh environments, characteristic of fluoropolymers. It is widely used in the chemical processing industry, in piping systems, vales, tanks (both molded and lined), and other areas where its combination of excellent mechanical properties and superb resistance to most chemicals make it an ideal material for fluid handling equipment. Increasingly important is use of PVDF as the base resin for long-life, exterior coatings on aluminum, steel, masonry, wood, and plastics.

The high dielectric loss and high dielectric constant of PVDF (8–9) both restrict its use in some electrical applications and provide superior performance in others. PVDF has very unusual piezoelectric and pyroelectric properties which are opening up many new applications with a very high value in use (see [Chapter 5](#)).

PVDFs cost, about the lowest of the melt-processible fluoropolymers, is an important advantage. Essentially all the common procedures available for thermoplastic polymers can be used with PVDF. Pennwalt Corp. is the leading producer and markets a full line of PVDF resins under the trade name of Kynar.

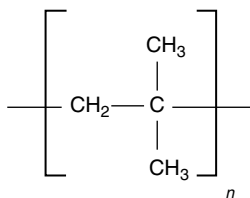
Perfluoroalkoxy (PFA) resins represent another class of commercially available class of melt-processable fluoroplastics. Their general chemical structure is



where $\text{R}_f = -\text{C}_n\text{F}_{2n+1}$.

PFA resin has somewhat better mechanical properties than FEP above 150°C and can be used up to 260°C . In chemical resistance it is about equal to PTFE. PFA resin is sold by Du Pont under the Teflon trademark.

4.2.1.7 Polyisobutylene

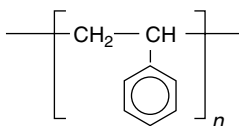


Monomer	Polymerization	Major Uses
Isobutylene	Cationic-initiated chain polymerization	Lubricating oils, sealants

High-molecular-weight polyisobutylene (PIB) is produced by cationic chain polymerization in methyl chloride solution at -70°C using aluminum chloride as the catalyst. Such polymers are currently available from Esso (Vistanex) and BASF (Oppanol).

PIB finds variety of uses. It is used as a motor oil additive to improve viscosity characteristics, as a blending agent for polyethylene to improve its impact strength and environmental stress-cracking resistance, as a base for chewing gum, as a tackifier for greases; it is also used in caulking compounds and tank linings. Because of its high cold flow, it has little use as a rubber in itself, but copolymers containing about 2% isoprene to introduce unsaturation for cross-linking are widely used (butyl rubber; see later).

4.2.1.8 Polystyrene



Monomer	Polymerization	Major Uses
Styrene	Free-radical-initiated chain polymerization	Packaging and containers (35%), housewares, toys and recreational equipment (25%), appliance parts (10%), disposable food containers (10%)

Polystyrene is made by bulk or suspension polymerization of styrene. Polystyrene is very low cost and is extensively used where price alone dictates. Its major characteristics [19,20] include rigidity, transparency, high refractive index, no taste, odor, or toxicity, good electrical insulation characteristics, low water absorption, and ease of coloring and processing. Polystyrene has excellent organic acid, alkali, salts, and lower alcohol resistance. It is, however, attacked by hydrocarbons, esters, ketones, and essential oils.

A more serious limitation of polystyrene in many applications is its brittleness. This limitation led to the development of rubber modified polystyrenes (containing usually 5–15% rubber), the so-called *high impact polystyrenes* (HIPS). The most commonly used are styrenebutadiene rubber and *cis*-1,4-polybutadiene.

The method of mixing the polystyrene and rubber has a profound effect on the properties of the product. Thus, much better results are obtained if the material is prepared by polymerization of styrene in the presence of the rubber rather than by simply blending the two polymers. The product of the former method contains not only polystyrene and straight rubber but also a graft copolymer in which polystyrene side chains are attached to the rubber.

Compared to straight or general-purpose polystyrenes, high-impact polystyrene materials have much greater toughness and impact strength, but clarity, softening point, and tensile strength are not as good. Expanded or foamed polystyrene (see [Chapter 2](#)), which has become very important as a thermal insulating material, has a low density, has a low weight cost, is less brittle, and can be made fire retarding.

End uses for all types of polystyrene are packaging, toys, and recreational products, housewares, bottles, lenses, novelties, electronic appliances, capacitor dielectrics, low-cost insulators, musical instrument reeds, light-duty industrial components, furniture, refrigeration, and building and construction uses (insulation).

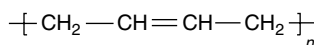
Packaging is by far the largest outlet: bottle caps, small jars and other injection-molded containers, blow-molded containers, toughened polystyrene liners (vacuum formed) for boxed goods, and oriented polystyrene film for foodstuffs are some of its uses.

The second important outlet is refrigeration equipment, including door liners and inner liners (made from toughened polystyrene sheet), molding for refrigerator furnishings, such as flip lids and trays, and expanded polystyrene for thermal insulation.

Expanded polystyrene products have widely increased the market for polystyrene resin (see the section on polystyrene foams in [Chapter 2](#)). With as light a weight as 2 lb/ft³ (0.032 g/cm³), the thermal conductivity of expanded polystyrene is very low, and its cushioning value is high. It is an ideal insulation and packaging material. Common applications include ice buckets, water coolers, wall panels, and general thermal insulation applications.

Packaging uses of expanded polystyrene range from thermoformed egg boxes and individually designed shipping packages for delicate equipment, such as cameras and electronic equipment, to individual beads (which may be about 1 cm in diameter and up to 5 cm long) for use as a loose fill material in packages.

4.2.1.9 Polybutadiene (Butadiene Rubber)



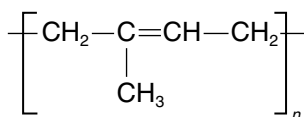
Monomer	Polymerization	Major Uses
Butadiene	Ziegler–Natta-catalyzed chain polymerization	Tires and tire products (90%)

Polybutadiene is made by solution polymerization of butadiene using Ziegler–Natta catalysts. Slight changes in catalyst composition produce drastic changes in the stereoregularity of the polymer. For example, polymers containing 97–98% of *trans*-1,4 structure can be produced by using Et₃Al/VCl₃ catalyst, those with 93–94% *cis*-1,4 structure by using Et₂AlCl/C₆OCl₂, and those with 90% 1,2-polybutadiene by using Et₃Al/Ti(OBu)₄. The stereochemical composition of polybutadiene is important if the product is to be used as a base polymer for further grafting. For example, a polybutadiene with 60% *trans*-1,4, 20% *cis*-1,4, and 20% 1,2 configuration is used in the manufacture of ABS resin.

Polybutadiene rubbers generally have a higher resilience than natural rubbers at room temperature, which is important in rubber applications. On the other hand, these rubbers have poor tear resistance, poor tack, and poor tensile strength. For this reason polybutadiene rubbers are usually used in conjunction with other materials for optimum combination of properties. For example, they are blended with natural rubber in the manufacture of truck tires and with styrene–butadiene rubber (SBR) in the manufacture of automobile tires.

Polybutadiene is also produced in low volume as specialty products. These include low-molecular-weight, liquid 1,2-polybutadienes (60–80%, 1,2 content) used as potting compounds for transformers and submersible electric motors and pumps, liquid *trans*-1,4-polybutadienes used in protective coatings inside metal cans, and hydroxy-terminated polybutadiene liquid resins for use as a binder and in polyurethane and epoxy resin formulations.

4.2.1.10 Polyisoprene

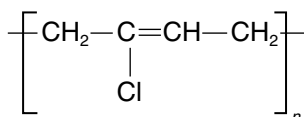


Monomer	Polymerization	Major Uses
Isoprene	Ziegler–Natta-catalyzed chain polymerization	Car tires (55%), mechanical goods, sporting goods, footwear, sealants, and caulking compounds

Polyisoprene is produced by solution polymerization using Ziegler–Natta catalysts. The *cis*-1,4-polyisoprene is a synthetic equivalent of natural rubber. However, the synthetic polyisoprenes have *cis* contents of only about 92–96%; consequently, these rubbers differ from natural rubber in several ways. The raw synthetic polyisoprene is softer than raw natural rubber (due to a reduced tendency for a stress-induced crystallization because of the lower *cis* content) and is therefore more difficult to mill. On the other hand, the unvulcanized synthetic material flows more readily; this feature makes it easier to injection mold. The synthetic product is somewhat more expensive than natural rubber.

Polyisoprene rubbers are used in the construction of automobile tire carcasses and inner liners and truck and bus tire treads. Other important applications are in mechanical goods, sporting goods, footwear, sealants, and caulking compounds.

4.2.1.11 Polychloroprene



Monomer	Polymerization	Major Uses
Chloroprene (2-chlorobuta-1,3-diene)	Free-radical-initiated chain polymerization (mostly emulsion polymerization)	Conveyor belts, hose, seals and gaskets, wire and cable sheathing

The polychloroprenes were first marketed by Du Pont in 1931. Today these materials are among the leading special-purpose or non-tire rubbers and are well known under such commercial names as Neoprene (Du Pont), Baypren (Bayer), and Butachlor (Distagul).

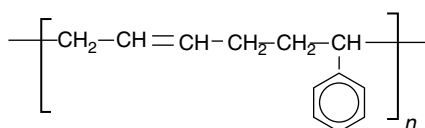
A comparison of polychloroprene and natural rubber or polyisoprene molecular structures shows close similarities. However, while the methyl groups activate the double bond in the polyisoprene molecule, the chlorine atom has the opposite effect in polychloroprene. Thus polychloroprene is less prone to oxygen and ozone attack than natural rubber is. At the same time accelerated sulfur vulcanization is also not a feasible proposition, and alternative vulcanization or curing systems are necessary.

Vulcanization of polychloroprene rubbers is achieved with a combination of zinc and magnesium oxide and added accelerators and antioxidants. The vulcanizates are broadly similar to those of natural rubber in physical strength and elasticity. However, the polychloroprene vulcanizates show much better heat resistance and have a high order of oil and solvent resistance (though less resistant than those of nitrile rubber). Aliphatic solvents have little effect, although aromatic and chlorinated solvents cause some swelling. Because of chlorine chloroprene rubber is generally self-extinguishing.

Because of their greater overall durability, chloroprene rubbers are used chiefly where a combination of deteriorating effects exists. Products commonly made of chloroprene rubber include conveyor belts, V-belts, diaphragms, hoses, seals, gaskets, and weather strips. Some important construction uses are highway joint seals, pipe gaskets, and bridge mounts and expansion joints. Latexes are used in gloves, balloons, foams, adhesives, and corrosion-resistant coatings.

4.2.2 Olefin Copolymers

4.2.2.1 Styrene–Butadiene Rubber



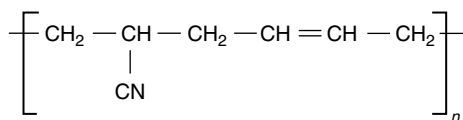
Monomer	Polymerization	Major Uses
Styrene, butadiene	Free-radical-initiated chain polymerization (mostly emulsion polymerization)	Tires and tread (65%), mechanical goods (15%), latex (10%), automotive mechanical good (5%)

In tonnage terms SBR is the worlds most important rubber [21,22]. Its market dominance is primarily due to three factors: low cost, good abrasion resistance, and a higher level of product uniformity than can be achieved with natural rubber.

Reinforcement of SBR with carbon black leads to vulcanizates which resemble those of natural rubber, and the two products are interchangeable in most applications. As with natural rubber, accelerated sulfur systems consisting of sulfur and an *activator* comprising a metal oxide (usually zinc oxide) and a fatty acid (commonly stearic acid) are used. A conventional curing system for SBR consists of 2.0 parts sulfur, 5.0 parts zinc oxide, 2.0 parts stearic acid, and 1.0 part *N-t*-butylbenzothiazole-2-sulfenide (TBBS) per 100 parts polymers.

The most important application of SBR is in car tires and tire products, but there is also widespread use of the rubber in mechanical and industrial goods. SBR latexes, which are emulsions of styrene–butadiene copolymers (containing about 23–25% styrene), are used for the manufacture of foam rubber backing for carpets and for adhesive and molded foam applications.

4.2.2.2 Nitrile Rubber



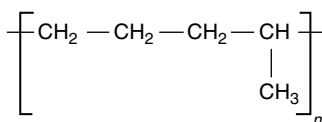
Monomer	Polymerization	Major Uses
Acrylonitrile, butadiene	Free-radical-initiated chain polymerization (mostly emulsion polymerization)	Gasoline hose, seals, gaskets, printing tools, adhesive, footwear

Nitrile rubber (acrylonitrile–butadiene copolymer) is a unique elastomer. The acrylonitrile content of the commercial elastomers ranges from 25% to 50% with 34% being a typical value. This non-hydrocarbon monomer imparts to the copolymer very good hydrocarbon oil and gasoline resistance. The oil resistance increases with increasing amounts of acrylonitrile in the copolymer. Nitrile rubber is also noted for its high strength and excellent resistance to abrasion, water, alcohols, and heat. Its drawbacks are poor dielectric properties and poor resistance to ozone.

Because of the diene component, nitrile rubbers can be vulcanized with sulfur. A conventional curing system consists of 2.5 parts sulfur, 5.0 parts zinc oxide, 2.0 parts stearic acid, and 0.6 parts *N-t*-butylbenzothiazole-2-sulfenamide (TBBS) per 100 parts polymer.

Nitrile rubbers (vulcanized) are used almost invariably because of their resistance to hydrocarbon oil and gasoline. They are, however, swollen by aromatic hydrocarbons and polar solvents such as chlorinated hydrocarbons, esters, and ketones.

4.2.2.3 Ethylene–Propylene–Elastomer



Monomer	Polymerization	Major Uses
Ethylene, propylene	Ziegler–Natta-catalyzed chain polymerization	Automotive parts, radiator and heater hoses, seals

Two types of ethylene–propylene elastomers are currently being produced; ethylene–propylene binary copolymers (EPM rubbers) and ethylene–propylene–diene ternary copolymers (EPDM rubbers).

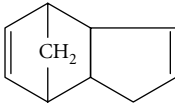
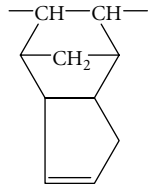
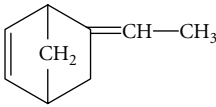
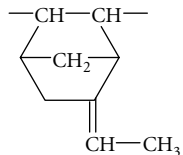
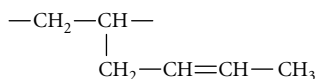
Because of their saturated structure, EPM rubbers cannot be vulcanized by using accelerated sulfur systems, and the less convenient vulcanization with free-radical generators (peroxide) is required. In contrast, EPDM rubbers are produced by polymerizing ethylene and propylene with a small amount (3–8%) of a diene monomer, which provides a cross-link site for accelerated vulcanization with sulfur.

A typical vulcanization system for EPDM rubber consists of 1.5 parts sulfur, 5.0 parts zinc oxide, 1.0 part stearic acid, 1.5 parts 2-mercaptobenzothiazole (MBT), and 0.5 part tetramethylthiuram disulfide (TMTD) per 100 parts polymer.

The EPDM rubbers, though hydrocarbon, differ significantly from the diene hydrocarbon rubbers considered earlier in that the level of unsaturation in the former is much lower, giving rubbers much better heat, oxygen, and ozone resistances. Dienes commonly used in EPDM rubbers include dicyclopentadiene, ethylidene norbornene, and hexa-1,4-diene (Table 4.5). Therefore the double bonds in the polymer are either on a side chain or as part of a ring in the main chain. Hence, should the double bond become broken, the main chain will remain substantially intact, which also accounts for the greater stability of the product.

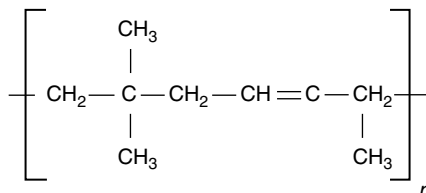
The use of EPDM rubbers for the manufacture of automobile and truck tires has not been successful, mainly because of poor tire cord adhesion and poor compatibility with most other rubbers. However, EPDM rubbers have become widely accepted as a moderately heat-resisting material with good weathering, oxygen, and ozone resistance. They find extensive use in nontire automobile applications, including body and chassis parts, car bumpers, radiator and heater hoses, weatherstrips, seals, and mats. Other applications include wire and cable insulation, appliance parts, hoses, gaskets and seals, and coated fabrics.

TABLE 4.5 Principal Diene Monomers Used in EPDM Manufacture

Monomer	Predominant Structure Present in Terpolymer
Dicyclopentadiene	 
4-Ethylidenenorborn-2-ene	 
Hexa-1,4-diene $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$	

These rubbers are now also being blended on a large scale with polyolefin plastics, particularly polypropylene, to produce an array of materials ranging from tough plastics at one end to the thermoplastic polyolefin rubbers (see later) at the other.

4.2.2.4 Butyl Rubber



Monomer	Polymerization	Major Uses
Isobutylene, isoprene	Cationic chain polymerization of isobutylene with 0.5–2.5 mol% of isoprene	Tire inner tubes and inner liners of tubeless tires (70%), inflatable sporting goods

Although polyisobutylene described earlier is a nonrubbery polymer exhibiting high cold flow, the copolymer containing about 2% isoprene can be vulcanized with a powerful accelerated sulfur system to give rubbery polymers. Being almost saturated, they are broadly similar to the EPDM rubbers in many properties.

The most outstanding property of butyl rubber is its very low air permeability, which has led to its extensive use in tire inner tubes and liners. A major disadvantage is its lack of compatibility with SBR, polybutadiene, and natural rubber. An ozoneresistant copolymer of isobutylene and cyclopentadiene has also been marketed.

4.2.2.5 Thermoplastic Elastomers

Monomer	Polymerization	Major Uses
Butadiene, isoprene, styrene	Anionic block polymerization	Footwear, automotive parts, hot-melt adhesives

Conventional rubbers are vulcanized, that is, cross-linked by primary valence bonding. For this reason vulcanized rubbers cannot dissolve or melt unless the network structure is irreversibly destroyed. These products cannot therefore be reprocessed like thermoplastics. Hence, if a polymer could be developed which showed rubbery properties at normal service temperatures but could be reprocessed like thermoplastics, it would be of great interest.

During the past three decades a few groups of materials have been developed that could be considered as being in this category. Designated as *thermoplastic elastomers*, they include (1) styrene–diene–styrene triblock copolymers; (2) thermoplastic polyester elastomers and thermoplastic polyurethane elastomers; and (3) thermoplastic polyolefin rubbers (polyolefin blends).

4.2.2.5.1 Styrene–Diene–Styrene Triblock Elastomers

The styrene–diene–styrene triblocks consist of a block of diene units joined at each end to a block of styrene units and are made by sequential anionic polymerization of styrene and a diene. In this way two important triblock copolymers have been produced—the styrene–butadiene–styrene (SBS) and styrene–isoprene–styrene (SIS) materials, developed by Shell.

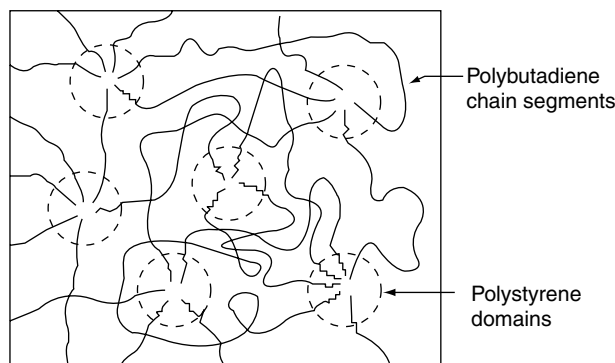


FIGURE 4.7 Schematic representation of polystyrene domain structure in styrene-butadiene-styrene triblock copolymers. (After Kaminsky, W. and Steiger, R. 1988. *Polyhedra*, 7(22), 2375.)

The commercial thermoplastic rubbers, Clarifex TR (Shell), are produced by joining styrene-butadiene or styrene-isoprene diblocks at the active ends by using a difunctional coupling agent. Similarly, copolymer molecules in the shape of a T, X, or star have been produced (e.g., Solprene by Phillips) by using coupling agents of higher functionality.

The outstanding behavior of these rubbers arises from the natural tendency of two polymer species to separate. However, this separation is restrained in these polymers since the blocks are covalently linked to each other. In a typical commercial SBS triblock copolymer with about 30% styrene content, the styrene blocks congregate into rigid, glassy domains which act effectively to link the butadiene segments into a network (Figure 4.7) analogous to that of cross-linked rubber.

As the SBS elastomers is heated above the glass transition temperature (T_g) of the polystyrene, the glass domains disappear and the polymer begins to flow like a thermoplastic. However, when the molten material is cooled (below T_g), the domains reharden and the material once again exhibits properties similar to those of a cross-linked rubber.

Below T_g of polystyrene the glassy domains also fulfill another useful role by acting like a reinforcing particulate filler. It is also an apparent consequence of this role that SBS polymers behave like carbon-black-reinforced elastomers with respect to tensile strength.

The styrene-diene-styrene triblock copolymers are not used extensively in traditional rubber applications because they show a high level of creep. The block copolymers can, however, be blended with many conventional thermoplastics such as polystyrene, polyethylene, and polypropylene, to obtain improved properties. A major area of use is in footwear, where blends of SBS and polystyrene have been used with remarkable success for crepe soles.

Other important uses are adhesives and coatings. A wide variety of resins, plasticizers, fillers, and other ingredients commonly used in adhesives and coatings can be used with styrene-diene-styrene triblock copolymers. With these ingredients properties such as tack, stiffness, softening temperatures, and cohesive strength can be varied over a wide range. With aliphatic resin additives the block copolymers are used for permanently tacky pressure-sensitive adhesives, and in conjunction with aromatic resins they are used for contact adhesives. The copolymers can be compounded into these adhesives by solution or hot-melt techniques.

The block copolymers are also used in a wide variety of sealants, including construction, industrial, and consumer-grade products. They are unique in that they can be formulated to produce a clear, water white product. Other applications include bookbinding and product assembly and chemical milling coatings.

4.2.2.5.2 Thermoplastic Polyester Elastomers

Because of the relatively low T_g of the short polystyrene blocks, the styrene–diene–styrene triblock elastomers have very limited heat resistance. One way to overcome this problem is to use a block copolymer in which one of the blocks is capable of crystallization and has a melting temperature well above room temperature. This approach coupled with polyester technology has led to the development of thermoplastic polyester elastomers (Hytrel by Du Pont and Arnitel by Akzo). A typical such polymer consists of relatively long sequences of *tetra*-methylene terephthalate (which segregate into rigid domains of high melting point) and softer segments of polyether (see Section 4.8 for more details).

Being polar polymers, these rubbers have good oil and gasoline resistance. They have a wider service temperature range than many general-purpose rubbers, and they also exhibit a high resilience, good flex fatigue resistance, and mechanical abuse resistance. These rubbers have therefore become widely accepted in such applications as seals, belting, water hose, etc.

4.2.2.5.3 Thermoplastic Polyurethane Elastomers

Closely related to the polyether–ester thermoplastic elastomers are thermoplastic polyurethane elastomers, which consist of polyurethane or urethane terminated polyurea hard blocks, with T_g above normal ambient temperature, separated by soft blocks of polyol, which in the mass are rubbery in nature (see Section 4.11 for more details). The main uses of thermoplastic rubbers (e.g., *Estane* by Goodrich) are for seals, bushes, convoluted bellows, and bearings.

One particular form of thermoplastic polyurethane elastomer is the elastic fiber known as Spandex. Several commercial materials of this type have been introduced, which include Lycra (Du Pont), Dorlastan (Bayer) Spanzelle (Courtaulds), and Vyrene (U.S. Rubber). Spandex fibers have higher modulus, tensile strength, and resistance to oxidation, and are able to produce finer deniers than natural rubber. They have enabled lighter-weight garments to be produced. Staple fiber blends of Spandex fiber with non-elastic fibers have also been introduced.

4.2.2.5.4 Thermoplastic Polyolefin Elastomers

Blends of EPDM rubbers with polypropylene in suitable ratios have been marketed as thermoplastic polyolefin rubbers. Their recoverable high elasticity is believed to be due to short propylene blocks in the EPDM rubber co-crystallizing with segments of the polypropylene molecules so that these crystalline domains act like cross-linking agents. Having good weathering properties, negligible toxicity hazards, and easy processability, these rubbers have received rapid acceptance for use in a large variety of nontire automotive applications such as bumper covers, headlight frames, radiator grilles, door gaskets, and other auto parts. They have also found use in cable insulation.

4.2.2.5.5 Ionic Elastomers

Ionic elastomers have been obtained using sulfonated EPDM. In one case an EPDM terpolymer consisting of 55% ethylene units, 40% propylene units, and 5% ethylidene norbornene units is sulfonated to introduce about 1 mol sulfonate groups (appended to some of the unsaturated groups of the EPDM). The sulfonic acid group is then neutralized with zinc acetate to form the zinc salt. The ionized sulfonic groups create ionic cross-links in the intermolecular structure (Figure 4.8), giving properties normally associated with a cross-linked elastomer. However, being a thermoplastic material, it can be processed in conventional molding machines. This rubber, however, has a very high melt viscosity, which must be reduced by using a polar flow promoter, such as zinc stearate, at levels of 9.5–19%.

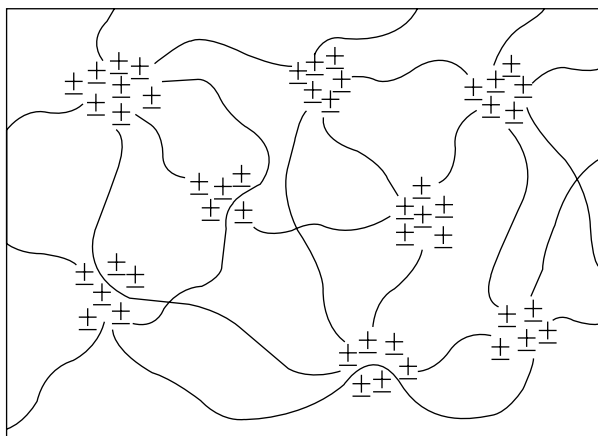


FIGURE 4.8 Schematic representation of domain structure in ionic elastomers.

4.2.2.6 Fluoroelastomers

Monomers	Polymerization	Major Uses
Vinylidene fluoride ($\text{CH}_2=\text{CF}_2$), chlorotrifluoroethylene ($\text{CF}_2=\text{CFCl}$), tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$), hexafluoropropylene ($\text{CF}_3\text{CF}=\text{CF}_2$), perfluoromethyl vinyl ether ($\text{CF}_2\text{CFOCF}_3$)	Free-radical-initiated chain polymerization	Aerospace industry (20%), industrial equipment, wire and cable jacketing, and other insulation applications

The fluoroelastomers are a general family of fluorinated olefin copolymers. To be rubbery, the copolymer must have a flexible backbone and be sufficiently irregular in structure to be noncrystalline. A number of important fluororubbers are based on vinylidene fluoride ($\text{CH}_2=\text{CF}_2$). Several common products are listed in Table 4.6.

TABLE 4.6 Commercial Fluoroelastomers

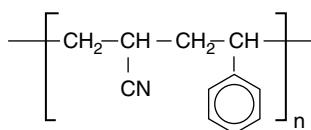
Composition	Trade Name (manufacturer)	Remarks
Vinylidene fluoride–hexafluoro- propylene copolymer	Viton A (Du Pont)	60–85% VF. Largest tonnage production among fluororubbers
	Fluorel (MMM)	
Vinylidene fluoride–hexafluoro- propylene–tetrafluoroethylene terpolymer	Viton B (Du Pont)	Superior resistance to heat, chemical, and solvent
	Daiel G-501 (Daikin Kogyo)	
Vinylidene fluoride–chlorotri- fluoroethylene copolymer	Kel-F 3700 (MMM)	Superior resistance to oxidizing acids
	Kel-F 5500 (MMM)	
Vinylidene fluoride–1-hydro- pentafluoropropylene– tetrafluoroethylene terpolymer	Tecnoflon T (Montecatini)	Superior resistance to oil, chemical, and solvent
Tetrafluoroethylene–perfluoro- (methyl vinyl ether) + cure site monomer terpolymer	Kalrez (Du Pont)	Excellent air oxidation resistance to 315°C
Tetrafluoroethylene–propylene cure site monomer ^a terpolymer	Aflas (Asahi Glass)	Cross-linked by peroxides. Resistant to inorganic acids and bases. Cheaper alternative to Kalrez

^a Suggested are triallyl cyanurate.

The most important of the above products are the copolymers of vinylidene fluoride and hexafluoropropylene (VF₂–HFP), as typified by the Du Pont product Viton A. The terpolymer of these two monomers together with tetrafluoroethylene (VF₂–HFP–TFE) is also of importance (e.g., Du Pont product Viton B). This terpolymer is the best among oil-resistant rubbers in its resistance to heat aging, although its actual strengths are lower than for some other rubbers. The copolymers of vinylidene fluoride and chlorotrifluoroethylene (VF₂–CTFE) are notable for their superior resistance to oxidizing acids such as fuming nitric acid.

Fluoroelastomers with no C–H groups will be expected to exhibit a higher thermal stability. Du Pont thus developed a terpolymer of tetrafluoroethylene, perfluoro(methyl vinyl ether) and, in small amounts, a cure site monomer of undisclosed composition. This product, marketed as Kalrez, has excellent air-oxidation resistance up to 315°C and exhibits extremely low swelling in a wide range of solvents, which is unmatched by any other commercial fluoroelastomer. Table 4.7 lists a number of commercial elastomers with their main properties and applications.

4.2.2.7 Styrene–Acrylonitrile Copolymer



Monomer	Polymerization	Major Uses
Acrylonitrile, styrene	Free-radical-initiated chain polymerization	Components of domestic appliances, electrical equipment and car equipment, picnic ware, housewares

Because of the polar nature of the acrylonitrile molecule, styrene–acrylonitrile (SAN) copolymers have better resistance to hydrocarbons, oils, and greases than polystyrene. These copolymers have a higher softening point, a much better resistance to stress cracking and crazing, and a higher impact strength than the homopolymer polystyrene, yet they retain the transparency of the latter. The toughness and chemical resistance of the copolymer increases with the acrylonitrile content but so do the difficulty in molding and the yellowness of the resin. Commercially available SAN copolymers have 20–30% acrylonitrile content. They are produced by emulsion, suspension, or continuous polymerization.

Due to their rigidity, transparency, and thermal stability, SAN resins have found applications for dials, knobs, and covers for domestic appliances, electrical equipment, car equipment, dishwasher-safe housewares, such as refrigerator meat and vegetable drawers, blender bowls, vacuum cleaner parts, humidifier parts, plus other industrial and domestic applications with requirements more stringent than can be met by polystyrene.

SAN resins are also reinforced with glass to make dashboard components and battery cases. Over 35% of the total SAN production is used in the manufacture of ABS blends.

4.2.2.8 Acrylonitrile–Butadiene–Styrene Terpolymer

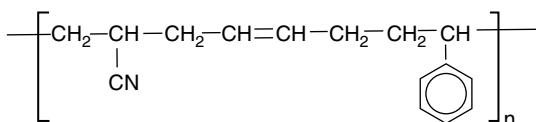


TABLE 4.7 Commercial Elastomer Products

Type	Properties	Major Uses
Natural rubber	Excellent properties of vulcanizates under conditions not demanding high levels of heat, oil, and chemical resistance	Tires, bushings, couplings, seals, footwear and belting; second place in global tonnage
Styrene–butadiene (SBR)	Reinforcement with carbon black leads to vulcanizates which resemble those of natural rubber; more effectively stabilized by antioxidants than natural rubber	Tires, tire products, footwear, wire and cable covering, adhesives; highest global tonnage
Polybutadiene	Higher resilience than similar natural rubber compounds, good low-temperature behavior and adhesion to metals, but poor tear resistance, poor tack, and poor tensile strength	Blends with natural rubber and SBR; manufacture of high-impact polystyrene
Polyisoprene	Similar to natural rubber, but excellent flow characteristics during molding	Tires, belting, footwear, flooring
Butyl	Outstanding air-retention property, but low resiliency and poor resistance to oils and fuels	Tire inner tubes, inner liners, seals, coated fabrics
Ethylene–propylene	Outstanding resistance to oxygen and ozone, poor fatigue resistance, poor tire-cord adhesion	Nontire automotive parts, radiator and heater hoses, wire and cable insulation
Nitrile	Excellent resistance to oils and solvents, poor low-temperature flexibility and poor resistance to weathering	Hoses, seals, gaskets, footwear
Chloroprene	High order of oil and solvent resistance (but less than nitrile rubber), good resistance to most chemicals, oxygen and ozone, good heat resistance, high strength but difficult to process	Mechanical automotive goods, conveyor belts, diaphragms, hose, seals and gaskets
Silicone	Outstanding electrical and high-temperature properties, retention of elasticity at low temperature, poor tear and abrasion resistance, relatively high price	Gaskets and sealing rings for jet engines, ducting, sealing strips, vibration dampers and insulation equipment in aircraft, cable insulation in naval craft, potting and encapsulation
Polyurethane	High tensile strength, tear, abrasion and oil resistance, relatively high price	Oil seals, shoe soles and heels, forklift truck tires, diaphragms, fiber coatings resistant to dry cleaning, variety of mechanical goods
Chlorosulfonated polyethylene	Very good heat, ozone, and weathering resistance, good resistance to oil and a wide range of chemicals, high elasticity, good abrasion resistance	Wire and cable coating, chemical plant hose, fabric coating, film sheeting, footwear, pond liners
Polysulfide	Excellent oil, solvent, and water resistance, high impermeability to gases, low strength, unpleasant odor (particularly during processing)	Adhesive, sealants, binders, hose
Epichlorohydrin	Low air permeability, low resilience, excellent ozone resistance, good heat resistance, flame resistance, and weathering resistance	Seals, gaskets, wire and cable coating
Fluoroelastomers	Outstanding heat resistance, superior oil, chemical, and solvent resistance, highest-priced elastomer	Aerospace applications, high quality seals, and gaskets

Monomers	Polymerization	Major Uses
Acrylonitrile, butadiene styrene	Free-radical-initiated chain polymerization	Pipe and fittings (30%), automotive and appliance (15%), telephones and business machine housings

A range of materials popularly referred to as ABS polymers first became available in the early 1950s. They are formed basically from three different monomers: acrylonitrile, butadiene, and styrene. Acrylonitrile contributes chemical resistance, heat resistance, and high strength; butadiene contributes toughness, impact strength, and low-temperature property retention; styrene contributes rigidity, surface appearance (gloss), and processability. Not only may the ratios of the monomers be varied, but the way in which they can be assembled into the final polymer can also be the subject of considerable variations. The range of possible ABS-type polymers is therefore very large [23].

The two most important ways of producing ABS polymers are (1) blends of styrene–acrylonitrile copolymers with butadiene–acrylonitrile rubber, and (2) interpolymers of polybutadiene with styrene and acrylonitrile, which is now the most important type. A typical blend would consist of 70 parts styrene–acrylonitrile (70:30) copolymer and 40 parts butadiene–acrylonitrile (65:35) rubber.

Interpolymers are produced by copolymerizing styrene and acrylonitrile in the presence of polybutadiene rubber (latex) by using batch or continuous emulsion polymerization. The resultant materials are a mixture of polybutadiene, SAN copolymer, and polybutadiene grafted with styrene and acrylonitrile. The mixture is made up of three phases: a continuous matrix of SAN, a dispersed phase of polybutadiene, and a boundary layer of SAN graft.

ABS polymers are processable by all techniques commonly used with thermoplastics. They are slightly hygroscopic and should be dried 2–4 h at 180–200°F (82–93°C) just prior to processing. A dehumidifying circulating air-hopper dryer is recommended. ABS can be hot stamped, painted, printed, vacuum metallized, electroplated, and embossed. Common fabrication techniques are applicable, including sawing, drilling, punching, riveting, bonding, and incorporating metal inserts and threaded and non-threaded fasteners. The machining characteristics of ABS are similar to those of nonferrous metals.

ABS materials are superior to the ordinary styrene products and are commonly described as tough, hard, and rigid. This combination is unusual for thermoplastics. Moreover, the molded specimens generally have a very good surface finish, and this property is particularly marked with the interpolymer type ABS polymers. Light weight and the ability to economically achieve a one-step finished appearance part have contributed to large-volume applications of ABS.

Adequate chemical resistance is present in the ABS materials for ordinary applications. They are affected little by water, alkalis, weak acids, and inorganic salts. Alcohol and hydrocarbon may affect the surfaces. ABS has poor resistance to outdoor UV light; significant changes in appearance and mechanical properties will result after exposure. Protective coatings can be applied to improve resistance to UV light.

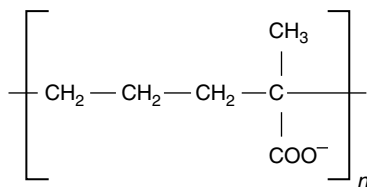
ABS materials are employed in thousand of applications, such as house-hold appliances, business machine and camera housings, telephone handsets, electrical hand tools (such as drill housings), handles, knobs, cams, bearings, wheels, gears, pump impellers, automotive trim and hardware, bathtubs, refrigerator liners, pipe and fittings, shower heads, and sporting goods. Business machines, consumer electronics, and telecommunications applications represent the fastest-growing areas for ABS. Painted, electroplated, and vacuum-metallized parts are used throughout the automotive, business machine, and electronics markets.

Multilayered laminates with an ABS outer layer can be produced by coextrusion. In this process two or three different polymers may be combined into a multilayered film or sheet. Adhesion is enhanced by cooling the extruded laminate directly from the melt rather than in a separate operation after the components of the sheet have been formed and cooled separately. In one process flows from individual extruders are combined in a *flow block* and then conveyed to a single manifold die. All the polymer streams should have approximately the same viscosity so that laminar flow can be maintained.

Multilayered films and sheets have the advantage that a chemically resistant sheet can be combined with a good barrier to oxygen and water diffusion, or a decorative glossy sheet can be placed over a tough, strong material. One commercial example is an ABS-high-impact-polystyrene sheet, which can be thermoformed (see [Chapter 2](#)) to make the inside door and food compartment of a refrigerator. Another example is a four-layered sheet comprising ABS, polyethylene, polystyrene, and rubber-modified polystyrene for butter and margarine packages. However, not all combinations adhere equally well, so there are limits to the design of such structures.

A variety of special ABS grades have been developed. These include high-temperature-resistant grades have been developed. (for automotive instrument panels, power tool housings), fire-retardant grades (for appliance housings, business machines, television cabinets), electroplating grades (for automotive grilles and exterior decorative trim), high-gloss, low-gloss, and matte-finish grades (for molding and extrusion applications), clear ABS grades (using methyl methacrylate as the fourth monomer), and structural foam grades (for molded parts with high strength-to-weight ratio). The structural foam grades are available for general purpose and flame-retardant applications. The cellular structure can be produced by injecting nitrogen gas into the melt just prior to entering the mold or by using chemical blowing agents in the resin (see also the section on [foaming processes](#) in Chapter 2).

4.2.2.9 Ethylene–Methacrylic Acid Copolymers (Ionomers)



Monomers	Polymerization	Major Uses
Ethylene, methacrylic acid	Free-radical-initiated chain polymerization	Packaging film, golf ball covers, automotive parts, footwear

4.2.2.9.1 Ionomers

Ionomer is a generic name for polymers containing interchain ionic bonding [24]. Introduced in 1964 by Du Pont, they have the characteristics of both thermoplastics and thermosetting materials and are derived by copolymerizing ethylene with a small amount (1–10% in the basic patent) of an unsaturated acid, such as methacrylic acid, using the high-pressure process. The carboxyl groups in the copolymer are then neutralized by monovalent and divalent cations, resulting in some form of ionic cross-links (see [Figure 4.8](#)) which are stable at normal ambient temperatures but which reversibly break down on heating. These materials thus process the advantage of cross-linking, such as enhanced toughness and stiffness, at ambient temperatures, but they behave as linear polymers at elevated temperatures, so they may be processed and even reprocessed without undue difficulty.

Copolymerization used in making ionomers has had the effect of depressing crystallinity, although not completely eliminating it, so the materials are also transparent. Ionomers also have excellent oil and grease resistance, excellent resistance to stress cracking, and a higher water vapor permeability than does polyethylene.

The principal uses of ionomers are for film lamination and coextrusion for composite food packaging. The ionomer resin provides an outer layer with good sealability and significantly greater puncture resistance than an LDPE film. Sporting goods utilize the high-impact toughness of ionomers. Most major golf ball manufacturers use covers of durable ionomer. Such covers are virtually cut proof in normal use

and retain a greater resiliency over a wider temperature range; they are superior to synthetic *trans*-polyisoprene in these respects.

Automotive uses (bumper pads and bumper guards) are based on impact toughness and paintability. In footwear applications, resilience and flex toughness of ionomers are advantages in box toes, counters, and shoe soles. Ski boot and ice skate manufacturers produce light weight outer shells of ionomers. Sheet and foamed sheet products include carpet mats, furniture tops, ski lift seat pads, boat bumpers, and wrestling mats.

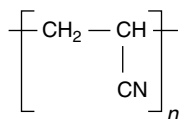
Ionomers should be differentiated from polyelectrolytes and ion-exchange resins, which also contain ionic groups. Polyelectrolytes show ionic dissociation in water and are used, among other things, as thickening agents. Common examples are sodium polyacrylate, ammonium poly-methacrylate (both anionic polyacrylate) and poly(*N*-butyl-4-vinyl-pyridinium bromide), a cationic polyelectrolyte. Ion-exchange resins used in water softening, in chromatography, and for various industrial purposes, are cross-linked polymers containing ionic groups.

Polyelectrolytes and ion-exchange resins are, in general, intractable materials and not processable on conventional plastics machinery. In ionomers, however, the amount of ionic bonding is limited to yield useful and tractable plastics. Using this principle, manufacturers can produce rubbers which undergo ionic cross-linking to give the effect of vulcanization as they cool on emergence from an extruder or in the mold of an injection-molding machine (see the section on thermoplastic polyolefin rubbers).

4.2.3 Acrylics

Acrylic polymers may be considered structurally as derivatives of acrylic acid and its homologues. The family of acrylics includes a range of commercial polymers based on acrylic acid, methacrylic acid, esters of acrylic acid and of methacrylic acid, acrylonitrile, acrylamide, and copolymers of these compounds. By far the best known applications of acrylics are acrylic fibers and acrylonitrile copolymers such as NBR, SAN, and ABS.

4.2.3.1 Polyacrylonitrile



Monomer	Polymerization	Major Uses
Acrylonitrile	Free-radical-initiated chain polymerization	Fibers in apparel (70%) and house furnishings (30%)

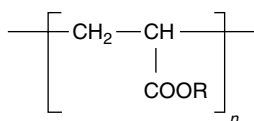
Polyacrylonitrile and closely related copolymers have found wide use as fibers [25]. The development of acrylic fibers started in the early 1930s in Germany. In the United States they were first produced commercially about 1950 by Du Pont (Orlon) and Monsanto (Acrilan).

In polyacrylonitrile appreciable electrostatic forces occur between the dipoles of adjacent nitrile groups on the same polymer molecule. This restricts the bond rotation and leads to a stiff, rodlike structure of the polymer chain. As a result, polyacrylonitrile has a very high crystalline melting point (317°C) and is soluble in only a few solvents, such as dimethylformamide and dimethylacetamide, and in concentrated aqueous solutions of inorganic salts, such as calcium thiocyanate, sodium perchlorate, and zinc chloride. Polyacrylonitrile cannot be melt processed because its decomposition temperature is close to the melting point. Fibers are therefore spun from solution by either wet or dry spinning (see [Chapter 2](#)).

Fibers prepared from straight polyacrylonitrile are difficult to dye. To improve dyeability, manufacturers invariably add to monomer feed minor amounts of one or two comonomers, such as methyl acrylate, methyl methacrylate, vinyl acetate, and 2-vinyl-pyridine. Small amounts of ionic monomers (sodium styrene sulfonate) are often included for better dyeability. Modacrylic fibers are composed of 35–85% acrylonitrile and contain comonomers, such as vinyl chloride, to improve fire retardancy.

Acrylic fibers are more durable than cotton, and they are the best alternative to wool for sweaters. A major portion of the acrylic fibers produced are used in apparel (primarily hosiery). Other uses include pile fabrics (for simulated fur), craft yarns, blankets, draperies, carpets, and rugs.

4.2.3.2 Polyacrylates



Monomer	Polymerization	Major Uses
Acrylic acid esters	Free-radical-initiated chain polymerization	Fiber modification, coatings, adhesives, paints

The properties of acrylic ester polymers depend largely on the type of alcohol from which the acrylic acid ester is prepared [26]. Solubility in oils and hydrocarbons increases as the length of the side chain increases. The lowest member of the series, poly(methyl acrylate), has poor low-temperature properties and is water sensitive. It is therefore restricted to such applications as textile sizes and leather finishes. Poly(ethyl acrylate) is used in fiber modifications and in coatings; and poly(butyl acrylate) and poly(2-ethylhexyl acrylate) are used in the formulation of paints and adhesives.

The original acrylate rubbers first introduced in 1948 by B. F. Goodrich and marketed as Hycar 4021 were a copolymer of ethyl acrylate with about 5% of 2-chloroethyl vinyl ether ($\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2-\text{CH}_2\text{Cl}$) acting as a cure site monomer. Such polymers are vulcanized through the chlorine atoms by amines (such as triethylenetetramine), which are, however, not easy to handle. Therefore, 2-chloroethyl vinyl ether has been replaced with other cure site monomers, such as vinyl and allyl chloroacetates; the increased reactivity of the chlorine in these monomers permits vulcanization with ammonium benzoate (which decomposes on heating to produce ammonia, the actual cross-linking agent) rather than amines.

Acrylate rubbers have good oil resistance. In heat resistance they are superior to most rubbers, exceptions being the fluororubbers, the fluororubbers, the silicones, and the fluorosilicones. It is these properties which account for the major use of acrylate rubbers, i.e., in oil seals for automobiles. They are, however, inferior in low-temperature properties.

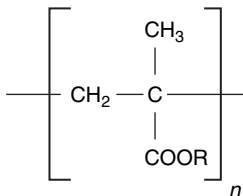
A few acrylate rubbers (such as Hycar 2121X38) are based on butyl acrylate. These materials are generally copolymers of butyl acrylate and acrylonitrile ($\sim 10\%$) and may be vulcanized with amines. They have improved low-temperature flexibility compared to ethyl acrylate copolymers but swell more in aromatic oils.

Ethylene copolymers with acrylates represent a significant segment of the ethylene copolymer market, as many LDPE producers use copolymerization as a strategy to obtain products more resistant to displacement by HDPE and LLDPE. Ethylene copolymers with methyl methacrylate and ethyl, butyl, and methyl acrylates are similar to EVA copolymers in properties (discussed later) but have improved thermal stability during extrusion and increased low-temperature flexibility.

The commercial products in this category generally contain 15–30% of the acrylate or methacrylate comonomer. Applications include medical packaging, disposable gloves, hoses, tubing, gaskets, cable insulation, and squeeze toys. Use of ethylene–ethyl acrylate copolymers for making vacuum cleaner hoses demonstrates the increased flexibility and long flex life that is possible with such materials.

Copolymers in which the acrylate monomer is the major component are useful as ethylene–acrylate elastomers (trade name: Vamac). These are terpolymers containing a small amount of an alkenoic acid to introduce sites ($C=C$) for subsequent cross-linking via reaction with primary diamines [see Equation 34 in Chapter 1]. These elastomers have excellent oil resistance and stability over a wide temperature range (-50°C to 200°C), being superior to chloroprene and nitrile rubbers. Although not superior to silicone and fluoroelastomers, they are less costly; uses include automotive (hydraulic systems seals, hoses) and wire and cable insulation.

4.2.3.3 Polymethacrylates



A large number of alkyl methacrylates, which may be considered as esters of poly(methacrylic acid), have been prepared [26]. By far the most important of these polymers is poly(methyl methacrylate), which is an established major plastics material. As with other linear polymers, the mechanical and thermal properties of polymethacrylates are largely determined by the intermolecular attraction, spatial symmetry, and chain stiffness.

As the size of the ester alkyl group increases in a series of poly(*n*-alkyl methacrylate)s, the polymer molecules become spaced further apart and the intermolecular attraction is reduced. Thus, as the length of the side chain increases, the softening point decreases, and the polymers become rubbery at progressively lower temperatures (Figure 4.9). However, when the number of carbon atoms in the side chain exceeds 12, the polymers become less rubbery, and the softening point, brittle point, and other

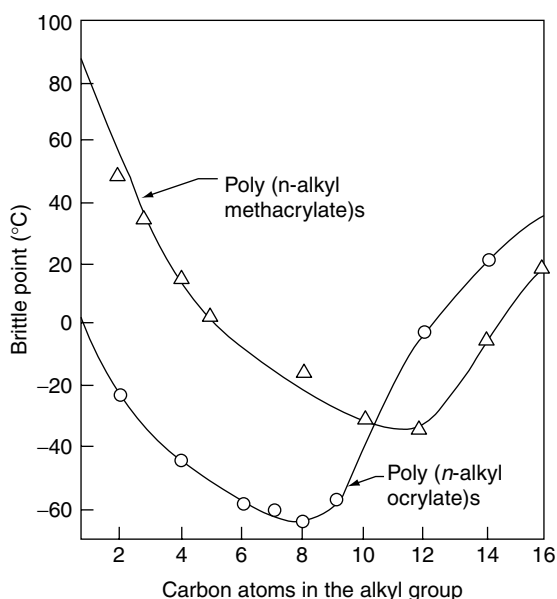


FIGURE 4.9 Brittle points of poly(*n*-alkyl acrylate)s and poly(*n*-alkyl methacrylate)s. (After Rehberg, C. E. and Fisher, C. H. 1948. *Ind. Eng. Chem.*, 40, 1431.)

TABLE 4.8 Vicat Softening Points of Polymethacrylates Derived from Monomers of Type $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOR}$

R—	Softening Point (°C)
CH_3-	119
CH_3-CH_2-	81
$\text{CH}_3-\text{CH}_2-\text{CH}_2-$	55
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-$	30
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$	— ^a
$(\text{CH}_3)_2\text{CH}-$	88
$(\text{CH}_3)_2\text{CH}-\text{CH}_2-$	67
$(\text{CH}_3)_3\text{C}-$	104
$(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}_2-$	46
$(\text{CH}_3)_3\text{C}-\text{CH}_2-$	115
$(\text{CH}_3)_3\text{C}-\text{CH}-$ CH_3	119

^a Too rubbery for testing.

properties related to the glass transition temperature rise with an increase in chain length (Table 4.8 and Table 4.9). As with the polyolefins, this effect is due to side-chain crystallization.

Poly(alkyl methacrylate)s in which the alkyl group is branched have higher softening points (see Table 4.8) and are harder than their unbranched isomers. This effect is not simply due to the better packing possible with the branched isomers. The lumpy branched structures impede rotation about the carbon-carbon bond on the main chain, thus contributing to stiffness of the molecule and consequently a higher transition temperature. Similarly, since the α -methyl group in polymethacrylates reduces chain flexibility, the lower polymethacrylates have higher softening points than the corresponding polyacrylates do.

Poly(methyl methacrylate (PMMA) is by far the predominant polymethacrylate used in rigid applications because it has crystal clear transparency, excellent weatherability (better than most other plastics), and a useful combination of stiffness, density, and moderate toughness. The glass transition temperature of the polymer is 105°C (221°F), and the heat deflection temperatures range from 75 to 100°C (167–212°F). The mechanical properties of PMMA can be further improved by orientation of heat-cast sheets.

PMMA is widely used for signs, glazing, lighting, fixtures, sanitary wares, solar panels, and automotive tail and stoplight lenses. The low index of refraction (1.49) and high degree of uniformity make PMMA an excellent lens material for optical applications.

Methyl methacrylate has been copolymerized with a wide variety of other monomers, such as acrylates, acrylonitrile, styrene, and butadiene. Copolymerization with styrene gives a material with improved melt-flow characteristics. Copolymerization with either butadiene or acrylonitrile, or blending PMMA with SBR, improves impact resistance. Butadiene-methyl methacrylate copolymer has been used in paper and board finishes.

TABLE 4.9 Glass Transition Temperatures of Polymethacrylates

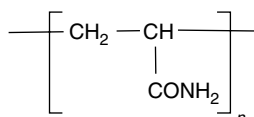
Ester Group	T_g (°C)
Methyl	105
Ethyl	65
<i>n</i> -Butyl	20
<i>n</i> -Decyl	–70
<i>n</i> -Hexadecyl	–9

Higher *n*-alkyl methacrylate polymers have commercial applications. Poly(*n*-butyl-), poly(*n*-octyl-) and poly(*n*-nonyl methacrylate)s are used as leather finishes; poly(lauryl methacrylate) is used to depress the pour point and improve the viscosity-temperature property of lubricating oils.

Mention may also be made here of the 2-hydroxyethyl ester of methacrylic acid, which is the monomer used for soft contact lenses. Copolymerization with ethylene glycol dimethacrylate produces a hydrophilic network polymer (a *hydrogel*). Hydrogel polymers are brittle and glassy when dry but become soft and plastic on swelling in water.

Terpolymers based on methyl methacrylate, butadiene, and styrene (MBS) are being increasingly used as tough transparent plastics and as additives for PVC.

4.2.3.4 Polyacrylamide



Monomer	Polymerization	Major Uses
Acrylamide	Free-radical-initiated chain polymerization	Flocculant, adhesives, paper treatment, water treatment, coatings

Polyacrylamide exhibits strong hydrogen bonding and water solubility. Most of the interest in this polymer is associated with this property. Polymerization of acrylamide monomer is usually conducted in an aqueous solution, using free-radical initiators and transfer agents.

Copolymerization with other water-soluble monomers is also carried out in a similar manner. Cationic polyacrylamides are obtained by copolymerizing with ionic monomers such as dimethylaminoethyl methacrylate, dialkyldimethylammonium chloride, and vinylbenzyltrimethylammonium chloride. These impart a positive charge to the molecule. Anionic character can be imparted by copolymerizing with monomers such as acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropanesulfonic acid, and sodium styrene sulfonate. Partial hydrolysis of polyacrylamide, which converts some of the amide groups to carboxylate ion, also results in anionic polyacrylamides.

Polyacrylamides have several properties which lead to a multitude of uses in diverse industries. Table 4.10 lists the main functions of the polymers and their uses in various industries.

Polyacrylamides are used as primary flocculants or coagulant aids in water clarification and mining application. They are effective for clarification of raw river water. The capacity of water clarifiers can be

TABLE 4.10 Applications of Polyacrylamide

Function	Application	Industry
Flocculation	Water clarification	General
	Waste removal	Sewage
	Solids recovery	Mining
	Retention aid	Paper
	Drainage aid	Paper
Adhesion	Dry strength	Paper
	Wallboard cementing	Construction
Rheology control	Waterflooding	Petroleum
	Viscous drag reduction	Petroleum
		Fire fighting
		Irrigation pumping

increased when the polymer is used as a secondary coagulant in conjunction with lime and ferric chloride. Polyacrylamides, and especially cationic polyacrylamides, are used for conditioning municipal and industries sludges for dewatering by porous and empty sand beds, vacuum filters, centrifuges, and other mechanical devices.

Certain anionic polyacrylamides are approved by the U.S. Environmental Protection Agency for clarification of potable water. Polymer treatment also allows filters to operate at higher hydraulic rates. The function of clarification is not explained by a simple mechanism. The long-chain linear polymer apparently functions to encompass a number of individual fine particles of the dispersed material in water, attaching itself to the particles at various sites by chemical bonds, electrostatic attraction, or other attractive forces. Relatively stable aggregates are thus produced, which be removed by filtration, settling, or other convenient means.

Polyacrylamides are useful in the paper industry as processing aids, in compounding and formulating, and as filler-retention aids. Polyacrylamides and copolymers of acrylamide and acrylic acid are used to increase the dry strength of paper.

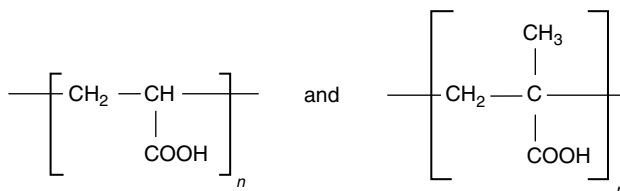
Polyacrylamides are used as flooding aids in secondary oil recovery from the producing oil well. Water, being of low viscosity, tends to finger ahead of the more viscous oil. However, addition of as little as 0.05% polyacrylamide to the waterflood reduces oil bypass and give significantly higher oil to water ratios at the producing wellhead. Greatly increased yields of oil result from adding polymer to waterflooding.

Solutions containing polyacrylamide are very slippery and can be used for water-based lubrication. Small amounts of polymer, when added to an aqueous solution, can significantly reduce the friction in pipes, thereby increasing the throughput or reducing the power consumption.

Other applications include additives in coatings and adhesives and binders for pigments.

Lightly cross-linked polyacrylamide is used to make superabsorbents of water. Astarch-g-polyacrylamide/clay superabsorbent composite has been synthesized [27] by graft copolymerization reaction of acrylamide, potato starch, and kaolinite micropowder ($<1\text{ }\mu\text{m}$) followed by hydrolysis with sodium hydroxide. Such a superabsorbent of compositin: 20% kaolinite, 20% potato starch, 60% acrylamide, 2% initiator (ceric amonium nitrate), and 0.04% cross-linker (*N,N*-methylenebisacrylamide) is found to absorb 2250 g $\text{H}_2\text{O/g}$ at room temperature at swelling equilibrium.

4.2.3.5 Poly(Acrylic Acid) and Poly(Methacrylic Acid)



Monomers	Polymerization	Major Uses
Acrylic acid and methacrylic acid	Free-radical-initiated chain polymerization	Sodium and ammonium-salts as polyelectrolytes, thickening agents

Poly(acrylic acid) and poly(methacrylic acid) may be prepared by direct polymerization of the appropriate monomer, namely, acrylic acid or methacrylic acid, by conventional free-radical techniques, with potassium persulfate used as the initiator and water as the solvent (in which the polymers are soluble); or if a solid polymer is required, a solvent such as benzene, in which the polymer is insoluble, can be used, with benzoyl peroxide as a suitable initiator.

The multitude of applications of poly(acrylic acid) and poly(methacrylic acid) is reminiscent of the fable of the man who blew on his hands to warm them and blew on his porridge to cool it. They are used as adhesives and release agents, as flocculants and dispersants, as thickeners and fluidizers, as reaction

inhibitors and promoters, as permanent coatings and removable coatings, etc. Such uses are the direct result of their varied physical properties and their reactivity. Many of the applications thus depend on the ability of these polymers to form complexes and to bond to substrates. Monovalent metal and ammonium salts of these polymers are generally soluble in water. These materials behave as anionic polyelectrolytes and are used for a variety of purposes, such as thickening agents, particularly for rubber latex.

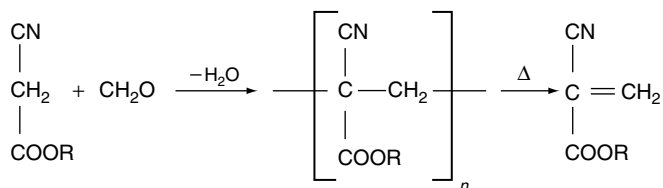
Superabsorbent polymers are loosely cross-linked networks of partially neutralized acrylic acid polymers capable of absorbing large amounts of water and retaining the absorbed water under pressure. Although superabsorbent polymers have been abundantly used in the disposable diaper industry for the past 30 years, their applications are still being expanded to many fields, including agriculture and horticulture, sealing composites, artificial snow, drilling fluid additives, drug delivery systems, and so on.

The swelling of a hydrophilic polymer is dependent on the rubbery elasticity, ionic osmotic pressure, and affinity of the polymer toward water. Although superabsorbent polymers have the greatest absorbency in water, the addition of an inorganic salt or organic solvent will reduce the absorbency.

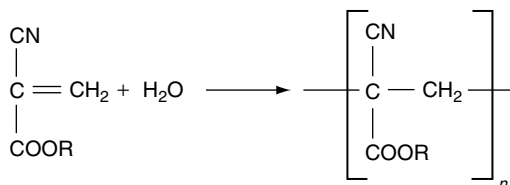
Clay and mineral fillers have been used for reducing production costs and improving the comprehensive water absorbing properties of superabsorbent materials. For example, a poly(acrylic acid)/mica superabsorbent has been synthesized with water absorbency higher than 1100 g H₂O/g. In a typical method of preparation, acrylic acid monomer is neutralized at ambient temperature with an amount of aqueous sodium hydroxide solution to achieve 65% neutralization (optimum). Dry ultrafine (<0.2 μm) mica powder (10 wt%) is added, followed by cross-linker *N,N*-methylene-bisacrylamide (0.10 wt%) and radical initiator, potassium persulfate. The mixture is heated to 60–70°C in a water bath for 4 h. The product is washed, dried under vacuum at 50°C, and screened.

4.2.3.6 Acrylic Adhesives

Acrylic adhesives are essentially acrylic monomers which achieve excellent bonding upon polymerization. Typical examples are cyanoacrylates and ethylene glycol dimethacrylates. Cyanoacrylates [28] are obtained by depolymerization of a condensation polymer derived from a malonic acid derivative and formaldehyde.



Cyanoacrylates are marketed as contact adhesives. Often popularly known as *superglue*, they have found numerous applications. In dry air and in the presence of polymerization inhibitors, methyl- and ethyl-2-cyanoacrylates have a storage life of many months. As with many acrylic monomers, air can inhibit or severely retard polymerization of cyanoacrylates. These monomers are, however, prone to anionic polymerization, and even a very weak base such as water can bring about rapid polymerization.



In practice, a trace of moisture occurring on a substrate is adequate to cause polymerization of the cyanoacrylate monomer to provide strong bonding within a few seconds of closing the joint and excluding air. Cyanoacrylate adhesives are particularly valuable because of their speed of action, which

obviates the need for complex jibs and fixtures. The amount of monomer applied should be minimal to obtain a strong joint. Larger amounts only reduce the strength. Notable uses of cyanoacrylates include surgical glue and dental sealants; morticians use them to seal eyes and lips.

Dimethacrylates, such as tetramethylene glycol dimethacrylate, are used as *anaerobic adhesives*. Air inhibition of polymerization of acrylic monomers is used to advantage in this application because the monomers are supplied along with a curing system (comprising a peroxide and an amine) as part of a one-part pack. When this adhesive is placed between mild steel surfaces, air inhibition is prevented since the air is excluded, and polymerization can take place. Though the metal on the surface acts as a polymerization promoter, it may be necessary to use a primer such as cobalt naphthenate to expedite the polymerization. The anaerobic adhesives are widely used for sealing nuts and bolts and for miscellaneous engineering purposes.

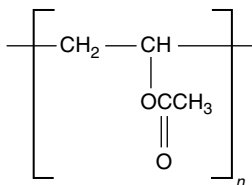
Dimethacrylates form highly cross-linked and, therefore, brittle polymers. To overcome brittleness, manufacturers often blend dimethacrylates with polyurethanes or other polymers such as low-molecular-weight vinyl-terminated butadiene-acrylonitrile copolymers and chlorosulfonated polyethylene. The modified dimethacrylate systems provide tough adhesives with excellent properties. These can be formulated as two-component adhesives, the catalyst component being added just prior to use or applied separately to the surface to be bonded. One-component systems also have been formulated which can be conveniently cured by ultraviolet radiation.

4.2.4 Vinyl Polymers

If the R substituent in an olefin monomer ($\text{CH}_2=\text{CHR}$) is either hydrogen, alkyl, aryl, or halogen, the corresponding polymer in the present discussion is grouped under polyolefins. If the R is a cyanide group or a carboxylic group or its ester or amide, the substance is an *acrylic* polymer. *Vinyl* polymers include those polyolefins in which the R substituent in the olefin monomer is bonded to the unsaturated carbon through an oxygen atom (vinyl esters, vinyl ethers) or a nitrogen atom (vinyl pyrrolidone, vinyl carbazole).

Vinyl polymers constitute an important segment of the plastics industry. Depending on the specific physical and chemical properties, these polymers find use in adhesives, in treatments for paper and textiles, and in special applications. The commonly used commercial vinyl polymers are described next.

4.2.4.1 Poly(Vinyl Acetate)



Monomer	Polymerization	Major Uses
Vinyl acetate	Free-radical-initiated chain Polymerization (mainly emulsion polymerization)	Emulsion paints, adhesives, sizing

Since poly(vinyl acetate) is usually used in an emulsion form, it is manufactured primarily by free-radical-initiated emulsion polymerization. The polymer is too soft and shows excessive cold flow, which precludes its use in molded plastics. The reason is that the glass transition temperature of 28°C is either slightly above or (at various times) below the ambient temperatures.

Vinyl acetate polymers are extensively used in emulsion paints, as adhesives for textiles, paper, and wood, as a sizing material, and as a permanent starch. A number of commercial grades are available which differ in molecular weight and in the nature of comonomers (e.g., acrylate, maleate, fumarate) which are often used. Two vinyl acetate copolymers of particular interest to the plastics industry are EVA and vinyl chloride–vinyl acetate copolymers.

EVA copolymers represent the largest-volume segment of ethylene copolymer market and are the products of low-density polyethylene (LDPE) technology. Commercial preparation of EVA copolymer is based on the same process as LDPE with the addition of controlled comonomer stream into the reactor. EVA copolymers are thermoplastic materials consisting of an ethylene chain incorporating 5–20 mol% vinyl acetate (VA), in general. The VA produces a copolymer with lower crystallinity than conventional ethylene homopolymer.

These lower crystallinity resins have lower melting points and heat seal temperatures, along with reduced stiffness, tensile strength, and hardness. EVAs have greater clarity, low-temperature flexibility, stress-crack resistance, and impact strength than LDPE. EVA resins are more permeable to oxygen, water vapor, and carbon dioxide. Chemical resistance is similar to that of LDPE, with somewhat better resistance to oil and grease for EVA resins of higher VA content. The VA groups contribute to improved adhesion in extrusions or hot-melt adhesive formulations.

The outdoor stability of EVA resins is superior to that of LDPE by virtue of their greater flexibility. Addition of UV stabilizers can extend the outdoor life of clear compounds to three to five years, depending on the degree of exposure. Outdoor life expectancy is also enhanced by the addition of carbon black.

In addition to specialty applications involving film and adhesives production, EVA are used in a variety of molding, compounds, and extrusion applications. Some typical end uses include flexible hose and tubing, footwear components, toys and athletic goods, wire and cable compounding, extruded gaskets, molded automotive parts (such as energy-absorbing bumper components), cap and closure seals, and color concentrates. In footwear applications, EVA resins are used in canvas box toes and flocked or fabric-laminated contours. Foamed and cross-linked EVA is used in athletic or leisure shoe midsoles and in sandals.

With increasing VA content, EVA resin properties range from those of LDPE to those of highly plasticized PVC. High VA resins are soft and flexible, with excellent toughness and good stress-crack resistance. With EVA resins these properties are permanent and do not dissipate with time because of the loss of the liquid plasticizer. EVAs also have exceptional low temperature toughness and flexibility.

The EVA copolymers are slightly less flexible than normal rubber compounds but have the advantage of simpler processing since no vulcanization is necessary. The materials have thus been largely used in injection molding in place of plasticized PVC or vulcanized rubber. Typical applications include turntable mats, based pads for small items of office equipment, buttons, car door protection strips, and for other parts where a soft product of good appearance is required.

A substantial use of EVA copolymers is as was additives and additives for hot-melt coatings and adhesives. Cellular cross-linked EVA copolymers are used in shoe parts.

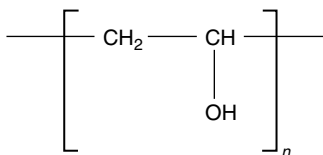
EVA copolymers with only a small vinyl acetate content (~ 3 mol%) are best considered as a modification of low-density polyethylene. These copolymers have less crystallinity and greater flexibility, softness, and, in case of film, surface gloss.

EVA can be processed by all standard plastics processing techniques, including injection and blow molding, thermoforming, and extrusion into sheet and shapes. They accommodate high loadings of fillers, pigments, and carbon blacks. They are compatible with other thermoplastics, and thus are frequently used for impact modification and improvement of stress-crack resistance. This combination of properties makes EVA highly adaptable vehicles for color concentrates. EVA resins can be formulated with blowing agents and cross-linking to produce low density foams via compression molding.

Hydrolysis of EVA copolymers yields ethylene–vinyl alcohol copolymers (EVOH). EVOH has exceptional gas barrier properties as well as oil and organic solvent resistance. The poor moisture resistance of EVOH is overcome by coating, coextrusion, and lamination with other substrates.

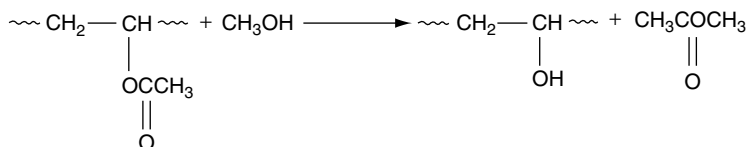
Applications include containers for food (ketchup, jelly, mayonnaise) as well as chemicals and solvents.

4.2.4.2 Poly(Vinyl Alcohol)



Manufacture	Major Uses
Alcoholysis of poly(vinyl acetate)	Paper sizing, textile sizing, cosmetics

Poly(vinyl alcohol) (PVA) is produced by alcoholysis of poly(vinyl acetate), because vinyl alcohol monomer does not exist in the free state [29]. (The term hydrolysis is often used incorrectly to describe this process.) Either acid or base catalysts may be employed for alcoholysis. Alkalien catalysts such as sodium hydroxide or sodium methoxide give more rapid alcoholysis. The degree of alcoholysis, and hence the residual acetate content, is controlled by varying the catalyst concentration.



The presence of hydroxyl groups attached to the main chain renders the polymer hydrophilic. PVA therefore dissolves in water to a greater or lesser extent according to the degree of hydrolysis. Polymers with a degree of hydrolysis in the range of 87–90% readily dissolve in cold water. Solubility decreases with an increase in the degree of hydrolysis, and fully hydrolyzed polymers are water soluble only at higher temperatures (> 85°C). This apparently anomalous behavior is due to the higher degree of crystallinity and the greater extent of hydrogen bonding in the completely hydrolyzed polymers.

Commercial PVA is available in a number grades which differ in molecular weight and degree of hydrolysis. The polymer finds a variety of uses. It functions as a nonionic surface active agent and is used in suspension polymerization as a protective colloid. It also serves as a binder and thickener and is widely used in adhesives, paper coatings, paper sizing, textile sizing, ceramics, and cosmetics.

Completely hydrolyzed grades of PVA find use in quick-setting, water-resistant adhesives. Combinations of fully hydrolyzed PVA and starch are used as a quick-setting adhesive for paper converting. Borated PVA, commonly called “tackified,” are combined with clay and used in adhesive applications requiring a high degree of wet tack. They are used extensively to glue two or more plies of paper together to form a variety of shapes such as tubes, cans, and cores.

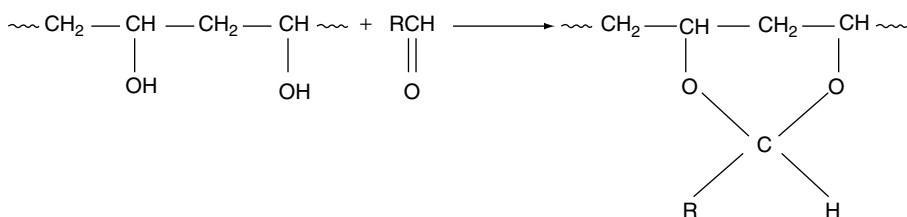
Since PVA film has little tendency to adhere to other plastics, it can be used to prevent sticking to mold. Films cast from aqueous solution of PVA are used as release agents in the manufacture of reinforced plastics.

Partially hydrolyzed grades have been developed for making tubular blown film (similar to that with polyethylene) for packages for bleaches, bath salts, insecticides, and disinfectants. Use of water-soluble PVA film for packaging preweighed quantities of such materials permits their addition to aqueous systems without breaking the package or removing the contents, thereby saving time and reducing material losses. Film made from PVA may be used for hospital laundry bags that are added directly to the washing machine.

A process has been developed in Japan for producing fibers from poly(vinyl alcohol). The polymer is wet spun from a warm aqueous solution into a concentrated aqueous solution of sodium sulfate containing sulfuric acid and formaldehyde, which insolubilizes the alcohol by formation of *formal* groups (see below). These fibers are generally known as *vinal* or *vinylon* fibers.

4.2.4.3 Poly(Vinyl Acetals)

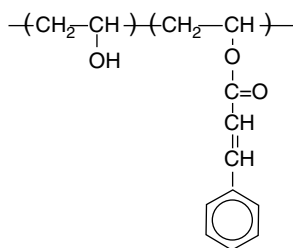
Poly(vinyl acetals) are produced by treating poly(vinyl alcohol) with aldehydes. (They may also be made directly from poly(vinyl acetate) without separating the alcohol.) Since the reaction with aldehyde involves a pair of neighboring hydroxyl groups on the polymer chain and the reaction occurs at random, some hydroxyl groups become isolated and remain unreacted. A poly(vinyl acetal) molecule will thus contain acetal groups and residual hydroxyl groups. In addition, there will be residual acetate groups due to incomplete hydrolysis of poly(vinyl acetate) to the poly(vinyl alcohol) used in the acetalization reaction. The relative proportions of these three types of groups may have a significant effect on specific properties of the polymer.



When the aldehyde in this reaction is formaldehyde, the product is poly(vinyl formal). This polymer is, however, made directly from poly(vinyl acetate) and formaldehyde without separating the alcohol. The product with low hydroxyl (5–6%) and acetate (9.5–13%) content (the balance being *formal*) is used in wire enamel and in structural adhesives (e.g., Redux). In both applications the polymer is used in conjunction with phenolic resins and is heat cured.

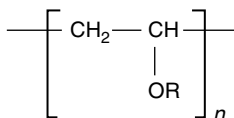
When the aldehyde in the acetalization reaction is butyraldehyde, i.e., $R = CH_3CH_2CH_2-$, the product is poly(vinyl butyral). Sulfuric acid is the catalyst in this reaction. Poly(vinyl butyral) is characterized by high adhesion to glass, toughness, light stability, clarity, and moisture insensitivity. It is therefore extensively used as an adhesive interlayer between glass plates in the manufacture of laminate safety glass and bullet-proof composition.

4.2.4.4 Poly(Vinyl Cinnamate)



Poly(vinyl cinnamate) is conveniently made by the Schotten–Baumann reaction using poly(vinyl alcohol) in sodium or potassium hydroxide solution and cinnamoyl chloride in methyl ethyl ketone. The product is, in effect, a copolymer of vinyl alcohol and vinyl cinnamate, as shown. The polymer has the ability to cross-link on exposure to light, which has led to its important applications in photography, lithography, and related fields as a *photoresist* (see also [Chapter 5](#)).

4.2.4.5 Poly(Vinyl Ethers)

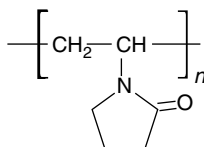


Commercial uses have developed for several poly(vinyl ethers) in which R is methyl, ethyl, and isobutyl. The vinyl alkyl ether monomers are produced from acetylene and the corresponding alcohols, and the polymerization is usually conducted by cationic initiation using Friedel–Craft-type catalysts.

Poly(vinyl methyl ether) is a water-soluble viscous liquid which has found application in the adhesive and rubber industries. One particular application has been as a heat sensitizer in the manufacture of rubber-latex dipped goods.

Ethyl and butyl derivatives have found uses as adhesives. *Pressure-sensitive adhesive tapes* made from poly(vinyl ethyl ether) incorporating antioxidants are said to have twice the shelf life of similar tapes made from natural rubber. Copolymers of vinyl isobutyl ether with vinyl chloride, vinyl acetate and ethyl acrylate are also produced.

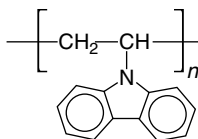
4.2.4.6 Poly(Vinyl Pyrrolidone)



Poly(vinyl pyrrolidone) is produced by free-radical-initiated chain polymerization of *N*-vinyl pyrrolidone. Polymerization is usually carried out in aqueous solution to produce a solution containing 30% polymer. The material is marketed in this form or spray dried to give a fine powder.

Poly(vinyl pyrrolidone) is a water-soluble polymer. Its main value is due to its ability to form loose addition compounds with many substances. It is thus used in cosmetics. The polymer has found several applications in textile treatment because of its affinity for dyestuffs. In an emergency it is used as a blood plasma substitute. Also, about 7% polymer added to whole blood allows it to be frozen, stored at liquid nitrogen temperatures for years, and thawed out without destroying blood cells.

4.2.4.7 Poly(Vinyl Carbazole)



Poly(vinyl carbazole) is produced by polymerization of vinyl carbazole using free-radical initiation or Ziegler–Natta catalysis.

Poly(vinyl carbazole) has a high softening point, excellent electrical insulating properties, and good photoconductivity, which has led to its application in xerography.

4.3 Part II: Condensation Polymers

According to the original classification of Carothers, condensation polymers are formed from bi- or polyfunctional monomers by reactions which involve elimination of some smaller molecule. A condensation polymer, according to this definition, is one in which the repeating unit lacks certain atoms which were present in the monomers(s) from which the polymer was formed.

With the development of polymer science and synthesis of newer polymers, this definition of condensation polymer was found to be inadequate. For example, in polyurethanes, which are classified as condensation polymers, the repeat unit has the same net composition as the two monomers—that is, a diol and a diisocyanate, which react without the elimination of any small molecule. Similarly the polymers produced by the ring-opening polymerization of cyclic monomers, such as cyclic ethers and amides, are generally classified as condensation polymers based on the presence of functional groups, such as the ether and amide linkages, in the polymer chains, even though the polymerization occurs without elimination of any small molecule.

To overcome such problems, an alternative definition has been introduced. According to this definition, polymers whose main chains consist entirely of C–C bonds are classified as *addition polymers*, whereas those in which heteroatoms (O, N, S, Si) are present in the polymer backbone are considered to be condensation polymers. A polymer which satisfies both the original definition (of Carothers) and the alternative definition or either of them, is classified as a condensation polymer. Phenol–formaldehyde condensation polymers, for example, satisfy the first definition but not the second.

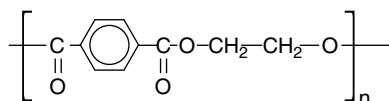
Condensation polymers described in Part II are classified as polyesters, polyamides, formaldehyde resins, polyurethanes, and ether polymers.

4.3.1 Polyesters

Polyesters were historically the first synthetic condensation polymers studied by Carothers in his pioneering work in the early 1930s. Commercial polyesters [30] were manufactured by polycondensation reactions, the methods commonly used being melt polymerization of diacid and diol, ester interchange of diester and diol, and interfacial polymerization (Schotten–Baumann reaction) of diacid chloride and diol. In a polycondensation reaction a by-product is generated which has to be removed as the reaction progresses.

Thermoplastic saturated polyesters are widely used in synthetic fibers and also in films and molding applications. The production of polyester fibers accounts for nearly 30% of the total amount of synthetic fibers. Unsaturated polyesters are mainly used in glass-fiber reinforced plastic products.

4.3.1.1 Poly(Ethylene Terephthalate)



Monomers	Polymerization	Major Uses
Dimethyl terephthalate or terephthalic acid, ethylene glycol	Bulk polycondensation	Apparel (61%), home furnishings (18%), tire cord (10%)

Whinfield and Dixon, in UK, developed polyethylene terephthalate fibers (Dacron, Terylene). This first Dacron polyester plant went into operation in 1953. *Ester interchange* (also known as *ester exchange* or *alcoholysis*) was once the preferred method for making polyethylene terephthalate (PET) because

dimethyl terephthalate can be readily purified to the high quality necessary for the production of the polymer. The process is carried out in two steps.

Dimethyl terephthalate (DMT) is reacted with excess ethylene glycol (mole ratio 1:2.1–2.2) at 150°C and 100 kPa (1 atm = 101 kPa). The output of the process is bis(hydroxyethyl) terephthalate (BHET). The pre-polymerization step (250–280°C, 2–3 kPa) follows in which BHET is polymerized to a degree of polymerization (DP) of up to 30. The next step is the polycondensation process where the DP is further increased to 100 by heating under vacuum, the process conditions being 280–290°C and 50–100 Pa. Up to this stage, PET is suitable for applications that do not require high molecular weight or high intrinsic viscosity $[\eta]$, such as fibers and sheets. Solid-state polymerization is used to further increase the DP to 150. The operating conditions are 200–240°C at 100 kPa and 5–25 h. Bottle-grade PET that has an $[\eta]$ of 0.73–0.81 dl g⁻¹ is normally produced by solid-state polymerization at 210°C for around 15–20 h [31].

In recent years methods have been developed to produce terephthalic acid with satisfactory purity, and direct polycondensation reaction with ethylene glycol is now the preferred route to this polymer.

Virgin PET is produced at different specifications because different applications require different properties [32]. Examples of intrinsic viscosity $[\eta]$ for different applications are recording tape 0.60, carbonated drink bottles 0.73–0.81, and industrial tire cord 0.85 dl g⁻¹. PET granules can be processed in many ways depending on application and final product requirements.

PET is widely used in synthetic fibers designed to simulate wool cotton, or rayon, depending on the processing conditions. They have good wash-and-wear properties and resistance to wrinkling. In the production of fiber the molten polymer is extruded through spinnerets and rapidly cooled in air. The filaments thus formed are, however, largely amorphous and weak. They are therefore drawn at a temperature (80°C) above T_g and finally heated at 190°C under tension, whereby maximum molecular orientation, crystallinity, and dimensional stability are achieved. The melting point of highly crystalline PET is 271°C.

Crystalline PET has good resistance to water and dilute mineral acids but is degraded by concentrated nitric and sulfuric acids. It is soluble at normal temperature only in proton donors which are capable of interaction with the ester group, such as chlorinated and fluorinated acetic acids, phenols, and anhydrous hydrofluoric acid.

PET is also used in film form (Melinex, Mylar) and as a molding material. The manufacture of PET film closely resembles the manufacture of fiber. The film is produced by quenching extruded sheet to the amorphous state and then reheating and stretching the sheet approximately threefold in the axial and transverse directions at 80–100°C. To stabilize the biaxially oriented film, it is annealed under restraint at 180–210°C. This operation increases the crystallinity of PET film and reduces its tendency to shrink on heating. The strength of PET in its oriented form is outstanding.

The principal uses of biaxially oriented PET film are in capacitors, in slot liners for motors, and for magnetic tape. Although a polar polymer, its electrical insulation properties at room temperature are good (even at high frequencies) because at room temperature, which is well below T_g (69°C), dipole orientation is severely restricted.

The high strength and dimensional stability of the polyester film have also led to its use for x-ray and photographic film and to a number of graphic art and drafting applications. The film is also used in food packaging, including boil-in-bag food pouches. Metallized polyester films have many uses as a decorative material.

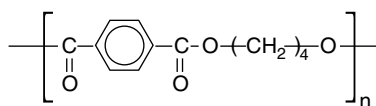
Because of its rather high glass transition temperature, only a limited amount of crystallization can occur during cooling after injection molding of PET. The idea of molding PET was thus for many years not a technical proposition. Toward the end of the 1970s Du Pont introduced Rynite, which is a PET nucleated with an ionomer, containing a plasticizer and only available in glass-fiber-filled form (at 30, 45, and 55% fill levels.) The material is very rigid, exceeding that of polysulfone, is less water sensitive than an unfilled polymer, and has a high heat-deflection temperature (227°C at 264 psi).

In the late 1970s the benefits of biaxial stretching PET were extended from film to bottle manufacture. Producing carbonated beverages PET bottles by blow molding has gained prominence (particularly in the United States) because PET has low permeability to carbon dioxide. The process has been extended,

particularly in Europe, to produce bottles for other purposes, such as fruit juice concentrates and sauces, wide-necked jars for coffee, and other materials. Because of its excellent thermal stability, PET is also used material for microwave and conventional ovens.

Virgin PET manufacturers have tended in recent years to produce PET copolymer, such as isophthalic acid modified PET, rather than homopolymer PET. PET bottles are normally made from copolymer PET because of its lower crystallinity, improved ductility, better process ability, and better clarity. Some of the most important PET copolymers are shown in Figure 4.10.

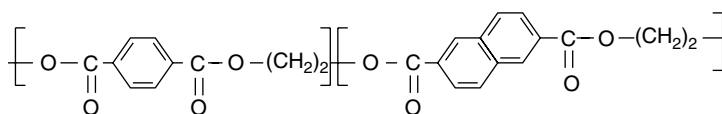
4.3.1.2 Poly(Butylene Terephthalate)



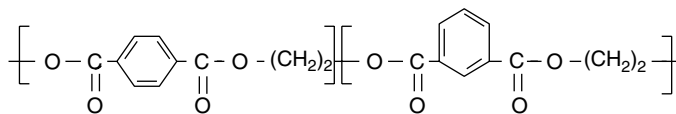
Monomers	Polymerization	Major Uses
Dimethyl terephthalate or terephthalic acid, butanediol	Bulk polycondensation	Machine parts, electrical applications, small appliances

Poly(butylene terephthalate), often abbreviated to PBT or PBTP, is manufactured by condensation polymerization of dimethyl terephthalate and butane-1,4-diol in the presence of tetrabutyl titanate. The polymer is also known as poly(tetramethylene terephthalate), PTMT in short. Some trade names for this engineering thermoplastic are Tenite PTMT (Eastman Kodak), Valox (General Electric), Celanex (Celanese) in America and Arnite PBTP (Akzo), Ultradur (BASF), Pocan (Bayer), and Crastin (Ciba-Geigy) in Europe.

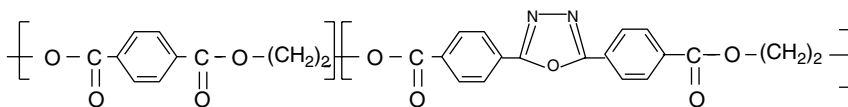
Because of the longer sequence of methylene groups in the repeating unit poly(butylene terephthalate) chains are both more flexible and less polar than poly(ethylene terephthalate). This leads to lower values for melting point (about 224°C) and glass transition temperature (22–43°C). The low glass



Poly[(ethylene terephthalate)-co-(ethylene 2,6-naphthalate)][PET/PEN]



Poly[(ethylene terephthalate)-co-(ethylene isophthalate)][PET/PEI]



Poly[(ethylene terephthalate)-co-(ethylene 2,5-bis(4-carboxyphenyl)1,3,4-oxadiazole)][PET/PEOD]

FIGURE 4.10 Some of the most important PET copolymers. (After Awaja, F, and Pavel, D. 2005. *Eur. Polymer J.*, 41, 1453. With permission.)

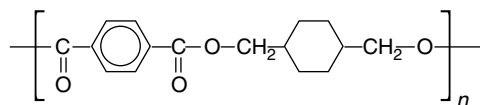
transition temperature facilitates rapid crystallization when cooling in the mold, and this allows short injection-molding cycles and high injection speeds.

PBT finds use as an engineering material due to its dimensional stability, particularly in water, and its resistance to hydrocarbon oils without showing stress cracking. PBT also has high mechanical strength and excellent electrical properties but a relatively low heat-deflection temperature 130°F (54°C) at 264 psi (1.8 MPa). The low water absorption of PBT—less than 0.1% after 24-h immersion—is outstanding. Both dimensional stability and electrical properties are retained under conditions of high humidity. The lubricity of the resin results in outstanding wear resistance.

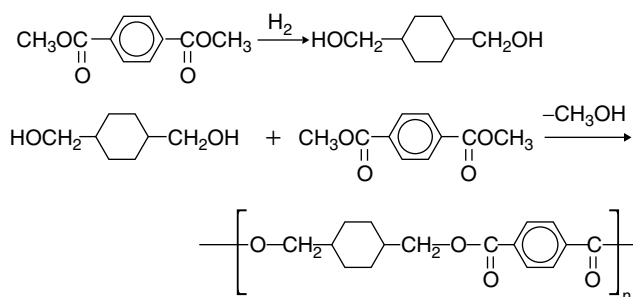
As with PET, there is particular interest in glass-filled grades of PBT. The glass has a profound effect on such properties as tensile strength, flexural modulus, and impact strength, as can be seen from the values of these properties for unfilled and 30% glass-filled PBT: 8200 vs. 17,000 psi (56 vs. 117 MPa), 340,000 vs. $1.1\text{--}1.2 \times 10^6$ psi (2350 vs. 7580–8270 MPa) and 0.8–1.0 vs. 1.3–1.6 ft.-lbf/in.² (Izod), respectively. Reinforcing with glass fiber also results in an increase in heat-deflection temperature to over 400°F (204°C) at 264 psi (1.8 MPa).

Typical applications of PBT include pump housings, impellers, bearing bushings, gear wheels, automotive exterior and under-the-hood parts, and electrical parts such as connectors and fuse cases.

4.3.1.3 Poly(Dihydroxymethylcyclohexyl Terephthalate)



In 1958, Eastman Kodak introduced a more hydrophobic polyester fiber under the trade name Kodel. The raw material for this polyester is dimethyl terephthalate. Reduction leads to 1,4-cyclohexylene glycol, which is used with dimethyl terephthalate in the polycondensation (ester exchange) reaction.



Eastman Kodak also introduced in 1972 a copolyester based on 1,4-cyclohexylene glycol and a mixture of terephthalic and isophthalic acids. The product is sold as Kodar PETG. Being irregular in structure, the polymer is amorphous and gives products of brilliant clarity.

In spite of the presence of the heterocyclic ring, the deflection temperature under load is as low as that of the poly(butylenes terephthalate)s, and the polymer can be thermoformed at draw ratios as high as 4:1 without blustering or embrittlement. Because of its good melt strength and low molding shrinkage, the material performs well in extrusion blow molding and in injection molding. The primary use for the copolymer is extrusion into film and sheeting for packaging.

Ethylene glycol-modified polyesters of the Kodel type are used in blow-molding applications to produce bottles for packaging liquid detergents, shampoos, and similar products. One such product is Kodar PETG 6703 in which one acid (terephthalic acid) is reacted with a mixture of glycols (ethylene glycol and 1,4-cyclohexylene glycol). A related glass-reinforced grade (Ektar PCTG) has also been offered.

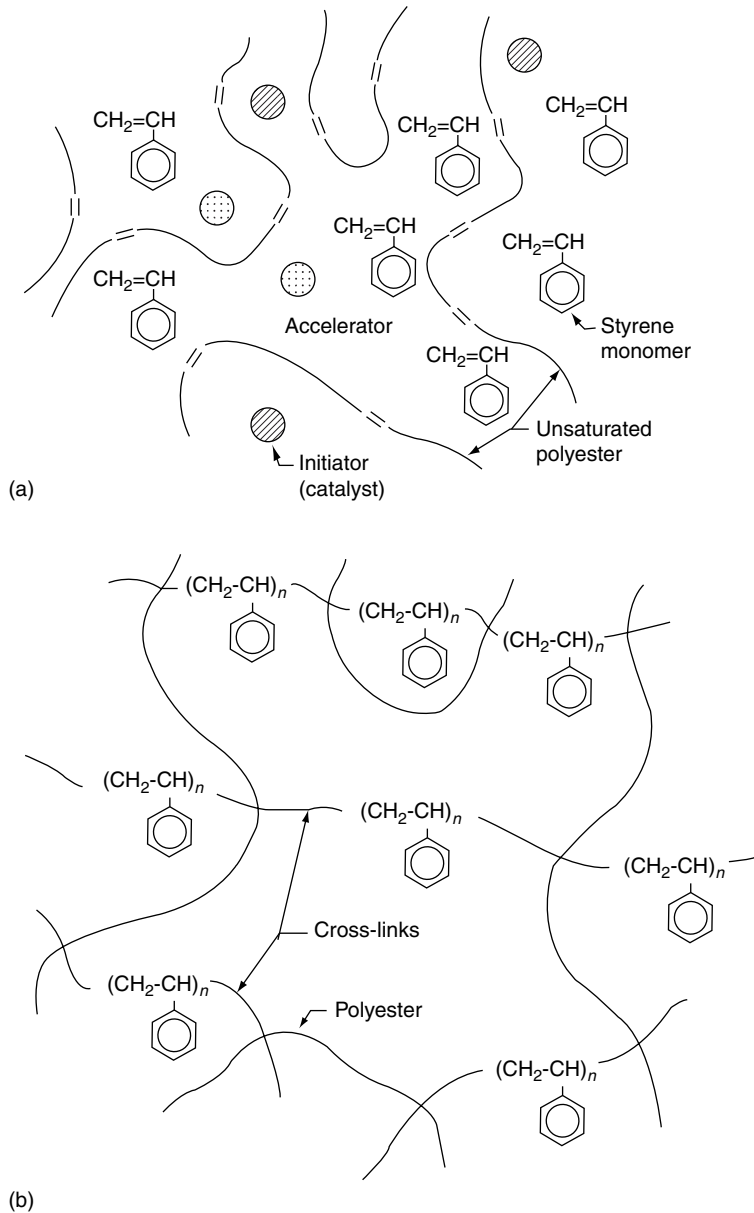


FIGURE 4.12 Curing of unsaturated polyesters. (a) Species in polyester resin ready for laminating. (b) Structures present in cured polyester resin. Cross-linking takes place via an addition copolymerization reaction. The value of $n \sim 2-3$ on average in general-purpose resins. (After Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.)

In practice, the peroxide curing system is blended into the resin before applying the resin to the reinforcement, which is usually glass fiber (E type), as perform, cloth, mat, or rovings, but sisal or more conventional fabrics may also be used. The curing system may be so varied (in both composition and quality) that curing times may range from a few minutes to several hours, and the cure may be arranged to proceed either at ambient or elevated temperatures.

The two most important peroxy materials used for room temperature curing of polyester resins are methyl ethyl ketone peroxide (MEKP) and cyclohexanone peroxide. These are used in conjunction with a cobalt compound such as a naphthenate, octoate, or other organic-solvent-soluble soap. The peroxides are referred to as *catalysts* (though, strictly speaking, these are polymerization initiators) and the cobalt compound is referred to as an *accelerator*.

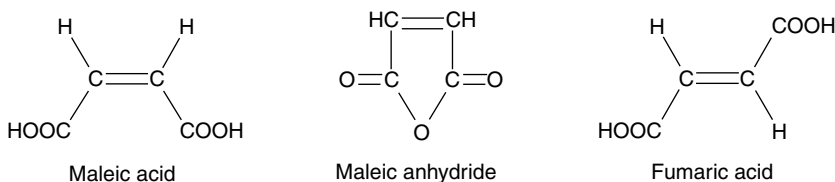
In room-temperature curing it is obviously necessary to add the resin to the reinforcement as soon as possible after the curing system has been blended and before gelation can occur. Benzoyl peroxide is most commonly used for elevated-temperature curing. It is generally supplied as a paste (~50%) in a liquid such as dimethyl phthalate to reduce explosion hazards and to facilitate mixing.

Since the cross-linking of polyester–styrene system occurs by a free-radical chain-reaction mechanism across the double bonds in the polyesters with styrene providing the cross-links, the curing reaction does not give rise to volatile by-products (unlike phenolic and amino resins) and it is thus possible to cure without applying pressure. This fact as well as that room temperature cures are also possible makes unsaturated polyesters most useful in the manufacture of large structures such as boats and car bodies.

Unsaturated polyesters find applications mainly in two ways: polyester–glass-fiber laminates and polyester molding compositions (discussed later).

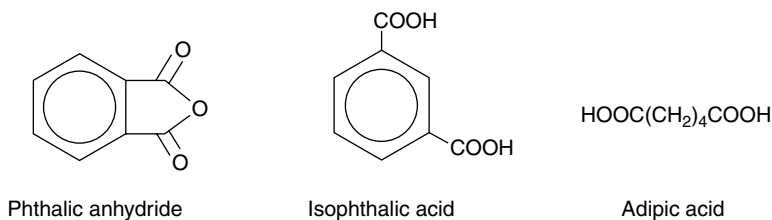
4.3.1.4.1 Raw Materials and Resin Preparation

General purpose resins generally employ either maleic acid (usually as the anhydride) or its *trans*-isomer fumaric acid as the unsaturated acid:



Maleic anhydride or fumaric acid confers the fundamental unsaturation to the polyester which provides the reactivity with coreactant monomers such as styrene. Maleic anhydride is a crystalline solid melting at 52.6°C (the acid melts at 130°C), while fumaric acid is a solid melting at 284°C. The latter is sometimes preferred to maleic anhydride because it is less corrosive, tends to give lighter colored products, higher impact strength, and slightly greater heat resistance.

Phthalic anhydride (melting point 131°C) is most commonly used to play the role of the saturated acid because it provides an inflexible link and maintains the rigidity in the cured resin. It is also preferred because its low price enables cheaper resins to be made. Use of isophthalic acid (melting point 347°C) in place of phthalic anhydride yields resins having higher heat distortion temperature and flexural moduli, better craze resistance, and often better water and alkali resistance. These resins are also useful in the preparation of resilient gel coats. Where a flexible resin is required, adipic acid may be used since, unlike the phthalic acids which give a rigid link, adipic acid gives highly flexible link and hence flexibility in the cured resin. Flexible resins are of value in gel coats.



Polyester laminating resins are manufactured by heating the component acids and glycols for several hours at 150–200°C in steel reactor vessels with moderate agitation to prevent local overheating and overhead condenser systems to collect the aqueous by-products, initially under ordinary pressure and, in

the last phase, under vacuum. To prevent discoloration and premature gelation caused by oxygen, the reactor is continuously purged with nitrogen or carbon dioxide. Reaction systems are fabricated from 304 or 316 stainless steels. Copper and brass valves and fittings are avoided because dissolved copper salts can affect the curing characteristics of the final resins.

A typical charge for a general purpose resin would be propylene glycol 170 parts, maleic anhydride 132 parts, and phthalic anhydride 100 parts, corresponding to molar ratios of 1.1: 0.67: 0.33. (The slight excess of glycol is primarily to allow for evaporation losses.) The glycols and dibasic acid can be substituted by other components of similar functionality, e.g., propylene glycol by ethylene and diethylene glycols, maleic anhydride by fumaric acid, and phthalic anhydride by isophthalic acid. A fusion-type reactor process, also known as *fusion-melt process*, is commonly used for condensing liquid glycols with dibasic acids of low melting temperature, including phthalic anhydride and aliphatic dibasic acids. The components are added in liquid form to facilitate loading, that is, glycol followed by molten anhydrides, thus saving the heating time needed when solid anhydrides are used. Heat is supplied by hot oil circulating through internal coils.

The polycondensation reaction occurs according to third-order kinetics with the progressive development of higher molecular weight polymers approaching an asymptotic limit. This requires extended reaction periods, e.g., 15 h at 190°C for phthalic resins to attain a satisfactory molecular weight. Steps must be taken to free the viscous melt of water, as the latter retards the reaction.

At 190°C, some glycol is vaporized and lost with the water of condensation. The reactors may be equipped with fractionating condenser systems to prevent this glycol loss. While the reaction rate is enhanced by acid catalysts, the latter also promote the formation of volatile ethers that are lost as by-products. A 5% excess glycol added to the initial charge compensates for glycol losses that may occur during the course of the reaction. Addition of glycol during the final stages is, however, not recommended.

The long reaction time in conventional fusion melt reactors, usually at temperatures above 180°C, causes the maleate ester to isomerize to the corresponding fumarate. This isomerization is of fundamental importance because the fumarate polymers display reactivities almost 20 times more than those of the maleate reaction products in subsequent polymerization reactions with styrene. The rate and extent of isomerization can be promoted at lower temperatures by a cycloaliphatic amine catalyst, e.g., morpholine.

The polyesterification reaction is followed by measuring the *acid number* (defined as the number of milligrams of potassium hydroxide equivalent to the acidity present in one gram of resin) of small samples periodically removed from the reactor. Where there are equimolar proportions of glycol and acid in the initial charge, the number average molecular weight is given by 5600/acid number. When the acid number value between 25 and 50 is reached, the heaters are switched off, the reactor is cooled to 150°C, and the contents transferred under vigorous agitation to a blend tank containing suitably inhibited styrene monomer at 30°C. The final temperature of the blend reaches about 80°C. At this temperature, even an inhibited styrenated resin polymerizes in several hours unless the blend is rapidly cooled to ambient temperature.

A mixture of inhibitors is commonly employed for the styrene diluent in order to obtain a balance of properties in respect of color, storage stability, and gelation rate of catalyzed resin. Thus, a typical composition of the diluent based on the above polyester formulation would be: styrene 172 parts, benzyltrimethylammonium chloride 0.44 part, hydroquinone 0.06 part, and quinone 0.006 part. After cooling to the ambient temperature, the resin is transferred into drums for storage and shipping.

Isophthalic acid is widely used as a substitute for phthalic anhydride since, as mentioned earlier, it improves certain properties of the cross-linked polymer. However, isophthalic acid is insoluble in the initial melt charge of maleic anhydride and propylene glycol and it also reacts more slowly with glycols than maleic anhydride. Thus while soluble components in the melt, namely, propylene glycol and maleic anhydride, react to form propylene glycol maleate polymers at lower temperatures (<190°C), isophthalic acid remains inert and requires heating subsequently to temperatures of 240°C to dissolve and react over prolonged periods, thus giving to rise to undesirable discoloration of the resin. Since

maleic anhydride has a preference to form esters with the more reactive primary hydroxyl group on the propylene glycol molecule, producing propylene glycol maleate esters with a preponderance of terminal secondary hydroxyl groups, subsequent condensation with isophthalic acid proceeds much more slowly than if the available hydroxyl functionality was primary, thus contributing to the slowness of transesterification reactions. Furthermore, sufficient unreacted isophthalic acid may be present in the final polymer, thus leading to precipitation upon blending with styrene and hence to a hazy resin product.

To reduce reaction time and eliminate color problems of one-step processes, as explained above, a two-step process is used to produce isophthalic resins. In the first stage, only the isophthalic acid is reacted with the glycol at a relatively high temperature, which may be elevated rapidly to over 220°C without concern for discoloration. Since ethylene glycol and propylene glycol boil at lower temperatures under ordinary pressure, the reactors must be provided with fractionating condensers or operated under pressure to prevent glycol loss. At 220°C, a clear melt is obtained from isophthalic acid and propylene glycol in about 8 h. However, esterification catalysts, such as tetrabutyl titanate, stannous oxalate, and dibutyl tin oxide can be used to accelerate the reaction.

At the end of the first stage, the melt is cooled to 150°C, maleic anhydride is added, and the temperature is raised to 180°C to re-start the process of condensation. The progress of the reaction is monitored by the measurement of carboxylic functionality and viscosity. As the reaction proceeds rapidly, the temperature only needs to be elevated to 210°C to drive the reaction. The stability of isophthalic acid esters at higher temperatures allows the development of polymers with higher molecular weight. (In contrast, high-molecular weight phthalic resins cannot be produced by the fusion melt process, since phthalic anhydride sublimates above 200°C.)

4.3.1.4.2 Polyester–Glass–Fiber Laminates (GRP, FRP)

Methods of producing FRP laminates with polyesters have been described in [Chapter 2](#). The major process today is the hand layup technique in which the resin is brushed or rolled into the glass mat (or cloth) by hand (see [Figure 2.44](#)). Since unsaturated polyesters are susceptible to polymerization inhibition by air, surfaces of the hand layup laminates may remain under-cured, soft, and, in some cases, tacky if freely exposed to air during the curing. A common way of avoiding this difficulty is to blend a small amount of paraffin wax (or other incompatible material) in with the resin. This blooms out on the surface and forms a protective layer over the resin during cure.

For mass production purposes, matched metal molding techniques involving higher temperatures and pressures are employed (see [Figure 2.45](#)). A number of intermediate techniques also exist involving vacuum bag, pressure bag, pultrusion, and filament winding (see [Figure 2.46](#) through [Figure 2.48](#)).

Glass fibers are the preferred form of reinforcement for polyester resins. Glass fibers are available in a number of forms, such as glass cloth, chopped strands, mats, or rovings (see “Glass Fibers” in [Chapter 2](#)). Some typical properties of polyester–glass laminates with different forms of glass reinforcements are given in [Table 4.11](#). It may be seen that laminates can have very high tensile strengths.

Being relatively cheaper, polyesters are preferred to epoxide and furan resins for general-purpose laminates. Polyesters thus account for no less than 95% of the low-pressure laminates produced. The largest single outlet is in sheeting for roofing and building insulation. For the greatest transparency of the laminate the refractive indices of glass-cured resins and binder should be identical.

The second major outlet is in land transport. Polyester–glass laminates are used in the building of sports car bodies, translucent roofing panel in lorries, and in public transport vehicles. In such applications the ability to construct large polyester–glass moldings without complicated equipment is used to advantage. Polyester resins in conjunction with glass cloth or mat are widely used in the manufacture of boat hulls up to 153 ft. (~46 m) in length. Such hulls are competitive in price and are easier to maintain and to repair [14].

The high strength-to-weight ratio, microwave transparency, and corrosion resistance of the laminates have led to their use in air transport applications as in aircraft radomes, ducting, spinners, and other parts. Land, sea, and air transport applications account for nearly half the polyester resin produced.

TABLE 4.11 Typical Properties of Polyester–Glass Laminates

Property	Mat Laminate (hand layup)	Mat Laminate (press formed)	Fine Square Woven Cloth Laminate	Rod from Rovings
Specific gravity	1.4–1.5	1.5–1.8	2.0	2.19
Tensile strength				
10^3 lbf/in. ²	8–17	18–25	30–45	150
MPa	55–117	124–173	210–310	1030
Flexural strength				
10^3 lbf/in. ²	10–20	20–27	40–55	155
MPa	69–138	138–190	267–380	1100
Flexural modulus				
10^5 lbf/in. ²	5	6	10–20	66
MPa	3440	4150	6890–1380	45,500
Dielectric constant (10^6 Hz)	3.2–4.5	3.2–4.5	3.6–4.2	—
Power factor (10^6 Hz)	0.02–0.08	0.02–0.08	0.02–0.05	Z—
Water absorption (%)	0.2–0.8	0.2–0.8	0.2–0.8	—

Source: From Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.

Other applications include such diverse items as chemical storage vessels, chemical plant components, swimming pools, stacking chairs, trays, and sports equipment.

4.3.1.4.3 Polyester Molding Compositions

Four types of polyester molding compounds may be recognized [14]: (1) dough-molding compound (DMC), (2) sheet-molding compound (SMC), (3) alkyd-molding compositions, sometimes referred to as *polyester alkyds*, (4) diallyl phthalate (DAP) and diallyl isophthalate (DAIP) compounds.

Dough-molding compounds of puttylike consistency are prepared by blending resins, catalyst, powdered mineral filler, reinforcing fiber (chopped strand), pigment, and lubricant in a dough mixer, usually of the Z-blade type. Formulations for three typical DMC grades are given in Table 4.12.

The tendency of thick sections of DMC structural parts to crack has been overcome by using low-profile polyester resins (or low-shrink resins). These are prepared by making a blend of a thermoplastic (e.g., acrylic) polymer–styrene system with a polyester–styrene system. Moldings of this blend cured at elevated temperatures exhibit negligible shrinkage and minimal warpage and have very smooth surface, to which paint may be applied with very little pretreatment.

A wide spectrum of properties may be obtained by varying the ratios of thermoplastics, polyester, and styrene in the blend. Among the thermoplastics quoted in the literature for such blending are poly(methyl methacrylate), polystyrene, PVC, and polyethylene. High-gloss DMCs using low-shrink resins have found uses in kitchen appliances such as toaster end plates, steam iron bases, and casings for electric heaters.

TABLE 4.12 Typical Formulations of DMC Grades

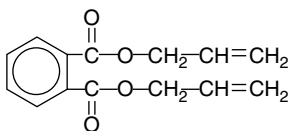
Ingredients	Low-Cost General-Purpose	High-Grade Mechanical	High-Grade Electrical
Polyester resin	100	100	100
E glass (1/4-in. length)	20	—	90
E glass (1/2-in. length)	—	85	—
Sisal	40	—	—
Calcium carbonate	240	150	—
Benzoyl peroxide	1	1	1
Pigment	2	2	2
Calcium stearate	2	2	2

Source: From Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.

Since the manufacture of DMC involves intensive shear that causes extensive damage to fibers, DMC moldings have less strength than GRP laminates. This problem is largely avoided with the sheet-molding compounds (SMC). In the SMC process, unsaturated polyester resin, curing systems, filler thickening agents, and lubricant are blended together and coated onto two polyethylene films. Chopped-glass rovings are supplied between the resin layers, which are then sandwiched together and compacted as shown in Figure 4.13. Thickening occurs by the reaction of free carboxyl end groups with magnesium oxide. This converts the soft, sticky mass to a handleable sheet, which takes usually a day or two. A typical formulation consists of 30% chopped-glass fiber, 30% ground limestone and resin. For molding, the sheet may be easily cut to the appropriate weight and shape and placed between the halves of the heated mold. The main applications of SMCs are in car parts, baths, and doors.

The polyester “alkyd” molding compositions are also based on a polyester resin similar to those used for laminating. (The term alkyd is derived from *alcohol* and *acid*.) They are prepared by blending the resin with cellulose pulp, mineral filler, pigments, lubricants, and peroxide curing systems on hot mills to the desired flow properties. The mix is then removed, cooled, crushed, and ground.

Diallyl phthalate (DAP) is a diester of phthalic acid and allyl alcohol and contains two double bonds.



On heating with a peroxide, DAP therefore polymerizes and eventually cross-links, forming an insoluble network polymer. However, it is possible to heat the DAP monomer under carefully controlled conditions, to give a soluble and stable partial polymer in the form of a white powder. The powder may then be blended with peroxide catalysts, fillers, and other ingredients to form a molding powder in the same manner as polyester alkyds. Similar products can be obtained from diallyl isophthalate (DAIP).

Both DAP and DAIP alkyd moldings are superior to the phenolics in their tracking resistance and in their availability in a wide range of colors; however, they tend to show a higher shrinkage on cure. The

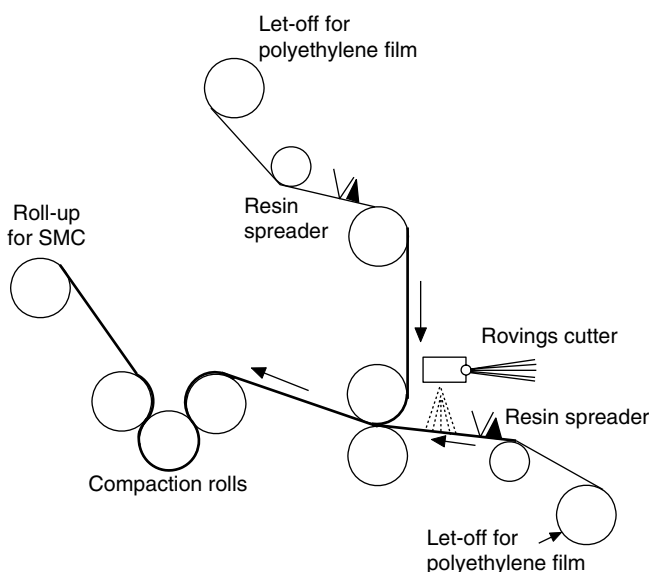


FIGURE 4.13 Schematic outline of machine used for sheet-molding compounds.

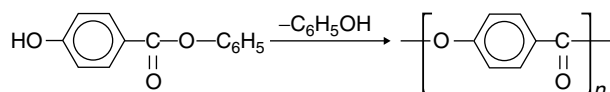
DAIP materials are more expensive than DAP but have better heat resistance. They are supposed to be able to withstand temperatures as high as 220°C for long periods.

The polyester alkyd resins are cheaper than the DAP alkyd resins but are mechanically weaker and do not maintain their electrical properties as well under severe humid conditions. Some pertinent properties of the polyester molding composition as compared in Table 4.13 along with those of a GP phenolic composition. The alkyd molding compositions are used almost entirely in electrical applications where the cheaper phenolic and amino resins are not suitable.

4.3.1.5 Aromatic Polyesters

Monomers	Polymerization	Major Uses
<i>p</i> -Hydroxy benzoic acid, bisphenol A, diphenyl isophthalate	Bulk polycondensation	High-temperature engineering thermoplastics, plasma coatings, abradable seals

In the 1960s the Carborundum Company introduced the homopolymer of *p*-hydroxybenzoic acid under the trade name Ekonol [35]. It is used in plasma coating. This wholly aromatic homopolyester is produced in practice by the self-ester exchange of the phenyl ester of *p*-hydroxybenzoic acid.



The homopolyester (mol. wt. 8000–12,000) is insoluble in dilute acids and bases and all solvents up to their boiling points. It melts at about 500°C and is difficult to fabricate. It can be shaped only by hammering (like a metal), by impact molding and by pressure sintering (420°C at 35 MPa). The difficulty in fabrication has severely limited the wider application of these polymers.

The homopolyester is available as a finely divided powder in several grades, based on particle size. The average particle size ranges from 35 to 80 μm. The material can be blended with various powdered

TABLE 4.13 Properties of Thermosetting Polyester Moldings

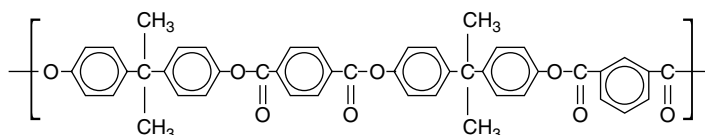
Property	Phenolic (GP)	DMC (GP)	Polyester Alkyd	DAP Alkyd	DAIP Alkyd
Molding temperature (°C)	150–170	140–165	140–165	150–165	150–165
Cure time (cup flow test) (sec)	60–70	25–40	20–30	60–90	60–90
Shrinkage (cm/cm)	0.007	0.004	0.009	0.009	0.006
Specific gravity	1.3	2.0	1.7	1.6	1.8
Impact strength (ft.-lb)	0.12–0.2	2.0–4.0	0.13–0.18	0.12–0.18	0.09–0.13
Volume resistivity (ohm-m)	10 ¹² –10 ¹⁴	10 ¹⁶	10 ¹⁶	10 ¹⁶	10 ¹⁶
Dielectric constant (10 ⁶ Hz)	4.5–5.5	5.6–6.0	4.5–5.0	3.5–5.0	4.0–6.0
Dielectric strength (90°C) (kV/cm)	39–97	78–117	94–135	117–156	117–156
Power factor (10 ⁶ Hz)	0.03–0.05	0.01–0.03	0.02–0.04	0.02–0.04	0.04–0.06
Water absorption (mg)	45–65	15–30	40–70	5–15	10–20

Source: Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.

metals, such as bronze, aluminum, and nickel-chrome, and is used in flame-spray compounds. Plasma-sprayed coatings are thermally stable, self-lubricating, and were and corrosion resistant. Applications include abradable seals for jet aircraft engine parts.

The polymer can also be blended up to 25% with PTFE. Such blends have good temperature and wear resistance and are self-lubricating. Applications include seals, bearings, and rotors.

Copolymeric aromatic polyesters, though possessing a somewhat lower level of heat resistance are easier to fabricate than are the wholly aromatic polymers; they also possess many properties that make them of interest as high-temperature materials. These materials, called *polyarylates*, are copolyester of terephthalic acid, and bisphenol A in the ratio of 1:1:2.



The use of two isomeric acids leads to an irregular chain which inhibits crystallization. This allows the polymer to be processed at much lower temperatures than would be possible with a crystalline homopolymer. Nevertheless the high aromatic content of these polyesters ensures a high T_g ($\sim 90^\circ\text{C}$). The polymer is self-extinguishing with a limiting oxygen index of 34 and a self-ignition temperature of 545°C . The heat-deflection temperature under load (1.8 MPa) is about 175°C .

Among other distinctive properties of the polyarylate are its good optical properties (luminous light transmission 84–88% with 1–2% haze, refractive index 1.61), high impact strength between that polycarbonate and polysulfone, exceptionally high level of recovery after deformation (important in applications such as clips and snap fasteners), good toughness at both elevated and low temperatures with very little notch sensitivity, and high abrasion resistance which is superior to that of polycarbonates.

Polyarylates weatherability and flammability (high oxygen index, low flame spread) are inherent and are achieved without additives. The weatherability properties therefore do not deteriorate significantly with time. (Tests show that over 5000 h of accelerated weathering results in virtually no change in performance with respect to luminous light transmittance, haze, gloss, yellowness, and impact.) Having no flame-retardant additives, the combustion products of polyarylate are only carbon dioxide, carbon monoxide, and water, with no formation of toxic gas.

Several companies have marketed polyarylates under the trade names: U-polymer (Unitika of Japan), Arylef (Solvay of Belgium), Ardel (Union Carbide), and Arylon (Du Pont). These are noncrystallizing copolymers of mixed phthalic acids with a bisphenol and have repeat units of the type shown above. They are melt processable with T_g and heat distortion temperatures in the range of 150 – 200°C and have similar mechanical properties to polycarbonate and polyethersulfones (see later).

The polymers are useful for electrical and mechanical components that require good heat resistance and for lighting fixtures and consumer goods that operate at elevated temperatures, such as microwave ovens and hair dryers. Potential uses of the somewhat cheaper arylon type polyesters include exterior car parts, such as body panels and bumpers. Typical properties of aromatic polyesters mentioned above are shown in Table 4.14.

A different approach to obtaining polymers with good melt processability coupled with high softening point has led to another type of aromatic copolyester, the so-called *liquid crystalline polymers* (LCPs) (see Chapter 5). In these polymers, marketed under the trade names Vectra (Celanese) and Xydar (Dartco Manufacturing), the retention of liquid crystalline order in the melt gives lower melt viscosities than would otherwise be achieved. Heat distortion temperatures are also in the high range of 180 – 240°C (Table 4.14). LCPs have thus heralded a new era of readily molded engineering and electrical parts for high temperature use.

4.3.1.6 Wholly Aromatic Copolyester

A high-performance, wholly aromatic copolyester suitable for injection molding was commercialized in late 1984 by Dartco Manufacturing under the trade name Xydar. Xydar injection-molding resins are based on terephthalic acid, *p,p'*-dihydroxybiphenyl, and *p*-hydroxybenzoic acid.

Polymers of this class contain long relatively rigid chains which are thought to undergo parallel ordering in the melt, resulting in low melt viscosity and good injection-molding characteristics, although at relatively high melt temperatures—750°F to 806°F (400–430°F) (400–430°C). The melt solidifies to form tightly packed fibrous chains in the molded parts, which give rise to exceptional physical properties. The tensile modulus of the molded unfilled resin is 2.4×10^6 psi (16,500 MPa) at room temperature and 1.2×10^6 psi (8300 MPa) at 575°F (300°C) tensile strength is about 20,000 psi (138 MPa), compressive strength is 6000 psi (41 MPa), and elongation is approximately 5%. Mechanical properties are claimed to improve at subzero temperatures.

The wholly aromatic copolyester is reported to have outstanding thermal oxidative stability, with a decomposition temperature in air of 1040 F (560°C) and 1053°F (567°C) in a nitrogen atmosphere. The resin is inherently flame retardant and does not sustain combustion. Its oxygen index is 42, and smoke generation is extremely low.

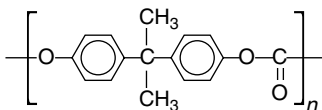
The resin is extremely inert, resists attack by virtually all chemicals, including acids, solvents, boiling water, and hydrocarbons. It is attacked by concentrated, boiling caustic but is unaffected by 30 days of immersion in 10% sodium hydroxide solution at 127°F (53°C). It withstands a high level of UV radiation and is transparent to microwaves.

The wholly aromatic copolyester for injection molding is available in filled and unfilled grades. It can be molded into thin-wall components at high speeds. The high melt flow also enables it to be molded into heavy-wall parts. No mold release is required because of the inherent lubricity and nonstick properties. No post-curing is necessary because the material is completely thermoplastic in nature. The material is expected to have many applications because of its moldability and its resistance to high temperatures, fire, and chemicals.

TABLE 4.14 Properties of Unfilled Aromatic Polyesters

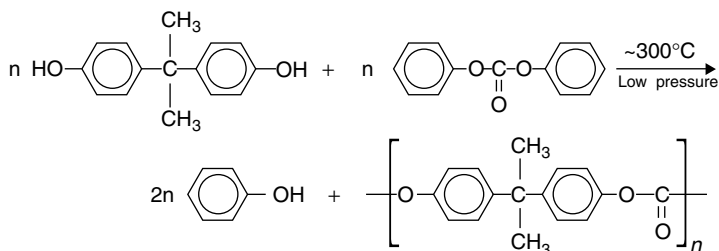
Property	Ekonol	Arylef or Ardel	Arylon	Vectra (Range for Various Grades)
Tensile strength				
10 ³ lbf/in. ²	11	10	10	20–35
MPa	74 (flexural)	70 (yield)	70	140–240
Elongation at break (%)	—	50	25	1.6–7
Tensile modulus				
10 ⁵ lbf/in. ²	—	3.0	2.9	14–58
GPa	—	2.1	2.0	10–40
Flexural modulus				
10 ⁵ lbf/in. ²	10	2.9	3.0	14–51
GPa	7.1	2.0	2.1	10–35
Heat distortion temperature (°C)	> 550	175	155	180–240
Impact strength, notched Izod				
ft.-lbf/in.	—	2.8–4.7	5.4	1–10
J/m	—	150–250	288	53–530
Limiting oxygen index (%)	—	34	26	35–50

4.3.1.7 Polycarbonates

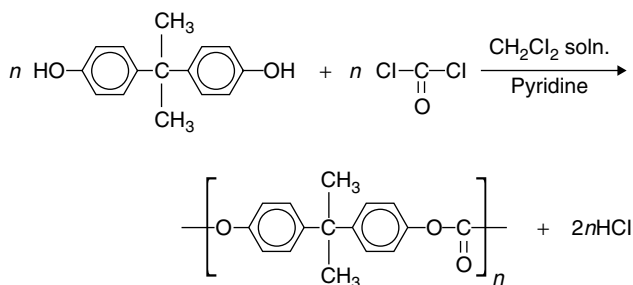


Monomers	Polymerization	Major Uses
Bisphenol A, phosgene	Interfacial polycondensation, solution polycondensation, transesterification	Glazing (37%), electrical and electronics (15%, appliances (15%), compact discs

The major processes for polycarbonate manufacture include (1) transesterification of bisphenol A with diphenyl carbonate [36,37]:



(2) solution phosgenation in the presence of an acid acceptor such as pyridine:



and (3) interfacial phosgenation in which the basic reaction is the same as in solution phosgenation, but it occurs at the interface of an aqueous phase and an organic phase. Here the acid acceptor is aqueous sodium hydroxide, which dissolves the bisphenol A and a monohydric phenol used for molecular-weight control (without which very high-molecular-weight polymers of little commercial value will be obtained), and the organic phase is a solvent for phosgene and the polymer formed. A mixture of methylene chloride and chlorobenzene is a suitable solvent. The interfacial polycondensation method is the most important process at present for the production of polycarbonate. Interestingly, polycarbonate represents the first commercial application of interfacial polycondensation. Fire-retardant grades of polycarbonates are produced by using tetrabromobisphenol A as comonomer.

Polycarbonate resin is easily processed by all thermoplastic-molding methods. Although it is most often injection molded or extruded into flat sheets, other options include blow molding, profile extrusion, and structural foam molding. Polycarbonate sheet can be readily thermoformed. The resin should be dried to less than 0.02% moisture before processing to prevent hydrolytic degradation at the high temperatures necessary for processing.

The chemical resistance of polyester materials is generally limited due to the comparative ease of hydrolysis of the ester groups, but the bisphenol A polycarbonates are somewhat more resistant. This resistance may be attributed to the shielding of the carbonate group by the hydrophobic benzene rings on either side. The resin thus shows resistance to dilute mineral acids; however, it has poor resistance to alkali and to aromatic and chlorinated hydrocarbons.

Polycarbonates have an unusual combination of high impact strength (12–16 ft.-lbf per inch notch for 1/2-in. \times 1/8-in. bar), heat-distortion temperature (132°C), transparency, very good electrical insulation characteristics, virtually self-extinguishing nature, and physiological inertness. As an illustration of the toughness of polycarbonate resins, it is claimed that an 1/8-in.-thick molded disc will stop a 22 caliber bullet, causing denting but not cracking. In creep resistance, polycarbonates are markedly superior to acetal and polyamide thermoplastics.

Because of a small dipole polarization effect, the dielectric constant of polycarbonates (e.g., 3.0 at 10^3 Hz) is somewhat higher than that for PTFE and the polyolefins (2.1–2.5 at 103 Hz). The dielectric constant is also almost unaffected by frequency changes up to 10^6 Hz and temperature changes over the normal range of operations. (Note that for satisfactory performance electrical insulating materials should have a *low* dielectric constant for *low* dissipation factor but *high* dielectric strength. For dielectrics used in capacitors, however, a high dielectric constant is desirable.)

At low frequencies (60 Hz) and in the ordinary temperature range (20–100°C), the power factor of polycarbonates (~ 0.0009) is remarkably low for a polar polymer. It increases, however, at higher frequencies, reaching a value of 0.010 at 10^6 Hz. The polycarbonates have a high volume resistivity (2.1×10^{20} ohm-cm at 23°C) and a high dielectric strength (400 kV/in., 1/8-in. sample). Because of the low water absorption, these properties are affected little by humidity. Polycarbonates, however, do have a poor resistance to tracking.

Although the electrical properties of polycarbonates are not as impressive as those observed with polyethylene, they are adequate for many purposes. These properties, coupled with the high impact strength, heat and flame resistance, transparency, and toughness have led to the extensive use of these resins in electronics and electrical engineering, which remains the largest single field of their application. Polycarbonate is the only material that can provide such a combination of properties, at least at a reasonable cost.

Known for many years, epoxy oligomers made from tetrabromobisphenol A are still used as the flame retardant in polycarbonates because they minimally affect the heat distortion temperature and even show a positive effect on impact strength. About 6–9 wt% of the epoxy oligomer is required for achieving V-0 rating and a thermotropic liquid crystal polyester helps to improve melt flow, so that thin-walled parts can be molded [38]. Antimony trioxide is not normally used in combination with halogen-containing additives in PC, because it causes loss of clarity.

At General Electric, it was found that very low additions (< 1 wt%) of alkali or alkaline earth metal salts of certain arylsulfonates provide self-extinguishing performance to PC. Potassium diphenylsulfone sulfonate, sodium trichlorobenzene sulfonate, and potassium perfluorobutane sulfonate are effective in PC at one-tenth of a per cent level and these salts are used on a commercial scale. The salts are mostly active in the condensed phase where they strongly destabilize PC upon heating, thus promoting fast decomposition and melt flow which removes heat.

Phosphate esters are rarely used in plain PC because of partial loss of clarity, tendency to stress-cracking, and somewhat reduced hydrolytic stability. However, aromatic phosphates are currently the products of choice for flame-retarding PC-based blends [39]. Triphenyl phosphate and mixed tri(*t*-butylphenyl phenyl) phosphate are reasonably effective in PC/ABS blends and are used commercially, though they have the disadvantage of relatively high volatility. However, bridged aromatic diphenyl phosphates, especially resorcinol bis(diphenyl phosphate) and bisphenol A bis(diphenyl phosphate), have found much broader application than monophosphates because of good thermal stability, high efficiency, and low volatility. Nano-scale inorganic materials have been shown to improve fire-retardant performance of aromatic phosphates and provide enhanced thermal dimensional stability for PC/ABS blends.

Polycarbonate covers for time switches, batteries, and relays utilize the good electrical insulation characteristics in conjunction with transparency, toughness, and flame resistance of the polymer. Its

combination of properties also accounts for its wide use in making coil formers. Many other electrical and electronic applications include moldings for computers, calculating machines and magnetic disc pack housing, contact strips, switch plates, and starter enclosures for fluorescent lamps. Polycarbonate films of high molecular weight are used in the manufacture of capacitors.

Traditional applications of polycarbonate in the medical market, such as filter housings, tubing connectors, and surgical staplers, have relied on the materials unique combination of strength, purity, transparency, and ability to stand all sterilization methods (steam, ethylene oxide gas, and gamma radiation). Polycarbonate-based blends and copolymers have further extended the materials usefulness to medical applications.

Recent years have seen a continuing growth of the market for polycarbonate glazing and light transmission units. Applications here include lenses and protective domes as well as glazing. The toughness and transparency of polycarbonates have led to many successful glazing applications of the polymer, such as bus shelters, telephone kiosks, gymnasium windows, lamp housings for street lighting, traffic lights, and automobiles, strip-lighting covers at ground level, safety goggles, riot-squad helmets, armor, and machine guards.

The limited scratch and weathering resistance of the polycarbonates is a serious drawback in these applications, and much effort is being directed at overcoming these problems. One approach is to coat the polycarbonate sheet with a glasslike composition by using a suitable priming material (e.g., *Margard*, marketed by the General Electric Company) to ensure good adhesion between coating and the base plastic.

Polycarbonates modified with ABS (acrylonitrile and styrene grafted onto polybutadiene) and MBS (methyl methacrylate and styrene grafted onto polybutadiene) resins have been available for many years. Usually used to the extent of 2–9%, the styrene-based terpolymers are claimed to reduce the notch sensitivity of the polycarbonate and to improve its resistance to environmental stress cracking while retaining from some grades the high impact strength of the unmodified polycarbonate. These materials find use in the electrical industry, in the automotive industry (instrument panels and glove compartment flaps), and for household appliances (coffee machine housings, hair drier housings, and steam handles). Elastomer modified polycarbonates have been used for automobile front ends and bumpers (e.g., 1982 Ford Sierra).

Polycarbonate is used for making compact audio discs, which are based on digital recording and playback technology and can store millions of bits of information in the form of minute pits in an area only which is read by the laser. Each “track” comprising a spiral of these pits is laid in polycarbonate which is backed with reflective aluminum and coated with a protective acrylic layer.

The processability of the polycarbonate, or any other material used as the substrate, is crucial in the manufacture of all optical discs. Bayers polycarbonate grade Makrolon CD-2000 has been specially developed to fit such requirements.

4.3.2 Polyamides

The early development of polyamides started with the work of W.H. Carothers and his colleagues, who, in 1935, first synthesized nylon-6,6—a polyamide of hexamethylene diamine and adipic acid—after extensive and classical researches into condensation polymerization.

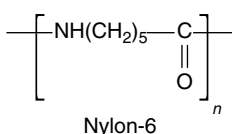
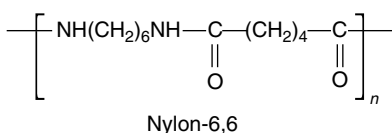
Commercial production of nylon-6,6 and its conversion into fibers was started by the Du Pont Company in 1939. In a parallel development in Germany, Schlack developed polyamides by ring-opening polymerization of cyclic lactams, and nylon-6 derived from caprolactam was introduced in 1939. Today nylon-6,6 and nylon-6 account for nearly all of the polyamides produced for fiber applications.

Nylon-6,6 and nylon-6 are also used for plastics applications. Besides these two polyamides, very many other aliphatic polyamides, have been prepared in the laboratory, and a few of them (nylon-11, nylon-12, and nylon-6,10 in particular) have attracted specialized interest as plastics materials. However, only about 10% of the nylons produced are used for plastics production. Virtually all of the rest goes for the production of fibers where the market is shared, roughly equally, between nylon-6 and nylon-6,6.

(Nylon is the trade name for the polyamides from unsubstituted, non-branched aliphatic monomers. A polyamide made from either an amino acid or a lactam is called nylon- x , where x is the number of carbon atoms in the repeating unit. A nylon made from a diamine and a dibasic acid is designated by two numbers, in which the first represents the number of carbons in the diamine chain and the second the number of carbons in the dibasic acid.)

For a variety of technical reasons the development of aromatic polyamides was much slower in comparison. Commercially introduced in 1961, the aromatic polyamides have expanded the maximum temperature well above 200°C. High-tenacity, high-modulus polyamide fibers (aramid fibers) have provided new levels of properties ideally suited for tire reinforcement. More recently there has been considerable interest in some new aromatic glassy polymers, in thermoplastic polyamide elastomers, and in a variety of other novel materials.

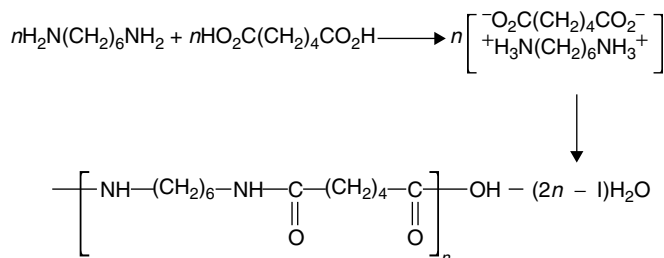
4.3.2.1 Aliphatic Polyamides



Monomers	Polymerization	Major Uses
Adipic acid, hexamethylenediamine, caprolactam	Bulk polycondensation	Home furnishings, apparel, tire cord

Aliphatic polyamides are produced commercially by condensation of diamines with dibasic acids, by self-condensation of an amino acid, or by self-condensation of an amino acid, or by ring-opening polymerization of a lactam [14,40,41]. To obtain polymers of high molecular weight, there should be stoichiometric equivalence of amine and acid groups of the monomers. For amino acids and lactams the stoichiometric balance is ensured by the use of pure monomers; for diamines and dibasic acids this is readily obtained by the preliminary formation of a 1:1 ammonium salt, often referred to as a *nylon salt*. Small quantities of monofunctional compounds are often used to control the molecular weight.

The nylon-6,6 salt (melting point 190–191°C) is prepared by reacting hexamethylenediamine and adipic acid in boiling methanol, so that the comparatively insoluble salt precipitates out. A 60% aqueous slurry of the salt together with a trace of acetic acid to limit the molecular weight to the desired level (9000–15,000) is heated under a nitrogen blanket at about 220°C in a closed autoclave under a pressure of about 20 atmospheres (atm). The polymerization proceeds to approximately 80–90% without removal of by-product water. The autoclave temperature is then raised to 270–300°C, and the steam is continuously driven off to drive the polymerization to completion.



The later stages of polymerization reaction constitute a melt *polycondensation*, since the reaction temperature is above the melting point of the polyamide. The molten polymer is extruded by nitrogen pressure on to a water-cooled casting wheel to form a ribbon which is subsequently disintegrated. In a continuous process for the production of nylon-6,6 similar reaction conditions are used, but the reaction mixture moves slowly through various zones of a reactor.

Nylon-6,10 is prepared from the salt (melting point 170°C) of hexamethylenediamine and sebacic acid by a similar technique. Nylon-6,9 uses azelaic acid. Decane-1,10-dicarboxylic acid is used for nylon-6,12.

In a typical batch process for the production of nylon-6 by ring-opening polymerization, a mixture of caprolactam, water (5–10% by weight), which acts as a catalyst, and a molecular-weight regulator [e.g., acetic acid ($\sim 0.1\%$)] is heated in a reactor under a nitrogen blanket at 250°C for above 12 h, a pressure of about 15 atm being maintained by venting off steam. The product consists of high-molecular-weight polymer (about 90%) and low-molecular-weight material (about 10%), which is mainly monomer. To obtain the best physical properties, the low-molecular-weight materials may be removed by leaching and/or by vacuum distillation.

In the continuous process, similar reaction conditions are used. In one process a mixture of molten caprolactam, water, and acetic acid is fed continuously to a reactor operating at about 260°C. Residence time is 18–20 h.

A simpler technique for the preparation of nylon-6 is the *polymerization casting* of caprolactam in situ in the mold. In this process rapid formation of polymer is achieved by anionic polymerization, initiated by strong bases such as metal amides, metal hydrides, and alkali metals. However, the anionic polymerization of lactams by strong bases alone is relatively slow because it is associated with an *induction period* due to a slow step in the initiation sequence leading to an *N*-acyl lactam which participates in the propagation reaction. The induction period may, however, be eliminated by adding along with the strong base a preformed *N*-acyl lactam or related compound at the start of the reaction.

A typical system for polymerization casting of caprolactam thus uses as a catalyst 0.1–1 mol% *N*-acetyl caprolactam and 0.15–0.50 mol% of the sodium salt of caprolactam. The reaction temperature is initially about 150°C, but during polymerization it rises to about 200°C. The technique is especially applicable to the production of large, complex shapes that could not be made by the more conventional plastics processing techniques.

Important advantages of the process are the low heats and low pressures involved. Although the polymerization process is exothermic, the relatively low heat of polymerization of caprolactam, coupled with its low melting point, makes the process easy to control and simplifies the heat transfer problem generally associated with the production of massive parts. Moldings of cast nylon-6 up to 1 tn are claimed to have been produced by these techniques.

Nylon parts made by polymerization casting of caprolactam exhibit higher molecular weights and a highly crystalline structure and are, therefore, slightly harder and stiffer than conventionally molded nylon-6.

Applications for cast nylon-6 include hug gears (e.g., a 150-kg nylon gear for driving a large steel drum drier) and bearings, gasoline and fuel tanks, buckets, building shutters, and various components for paper production machinery and mining and construction equipment. Later development has centered on adding reinforcing materials to the monomer before polymerization to produce parts with higher heat distortion temperature, impact strength and tensile strength.

Nylon-12 is produced by the ring-opening polymerization of lauro lactam (dodecyl lactam) such as by heating the lactam at about 300°C in the presence of aqueous phosphoric acid. Unlike the polymerization of caprolactam, the polymerization of dodecyl lactam does not involve an equilibrium reaction. Hence, an almost quantitative yield of nylon-12 polymer is obtained by the reaction, and the removal of low-molecular-weight material is unnecessary.

Nylon-11 is produced by the condensation polymerization of ω -aminoundecanoic acid at 200–220°C with continuous removal of water. The latter stages of the reaction are conducted under reduced pressure to drive the polymerization to completion.

Nylon copolymers can be obtained by heating a blend of two or more different nylons above the melting point so that amide interchange occurs. Initially, block copolymers are formed, but prolonged reaction leads to random copolymers. For example, a blend of nylon-6,6 and nylon-6,10 heated for 2 h gives a random copolymer (nylon-6,6–nylon-6,10) which is identical with a copolymer prepared directly from the mixed monomers. Other copolymers of this type are available commercially.

4.3.2.1.1 Properties

Aliphatic polyamides are linear polymers containing polar $-\text{CONH}-$ groups spaced at regular intervals by aliphatic chain segments. The principal structural difference between the various types of nylon is in the length of aliphatic chain segments separating the adjacent amide groups. The polar amide groups give rise to high interchain attraction in the crystalline zones, and the aliphatic segments impart a measure of chain flexibility in the amorphous zones. This combination of properties yields polymers which are tough above their glass transition temperatures.

The high intermolecular attraction also accounts for high melting points of nylons, which are usually more than 200°C. The melting point, however, decreases (which facilitates processing) as the length of the aliphatic segment in the chain increases, as indicated in Table 4.15.

Because of the high cohesive energy and their crystalline state, the nylons are resistant to most solvents. They have exceptionally good resistance to hydrocarbons and are affected little by esters, alkyl halides, and glycols. There are only a few solvents for the nylons, of which the most common are formic acid, glacial acetic acid, phenols, and cresols. Alcohols generally have some swelling action and may dissolve some copolymers (e.g., nylon-6,6, nylon-6,10, nylon-6). Nylons have very good resistance to alkalis at room temperature. Mineral acids attack nylons, but the rate of attack depends on the nature and concentration of acids and the type of nylon. Nitric acid is generally active at all concentrations.

Because of the presence of amide groups, the nylons absorb water. Figure 4.14 shows how the equilibrium water absorption of different nylons varies with humidity at room temperature, and Figure 4.15 shows how the rate of moisture absorption of nylon-6,6 is affected by the environmental conditions. Since dimensional changes may occur as a result of water absorption this effect should be considered when dimensional accuracy is required in a specific application. Manufacturers commonly supply data on the dimensional changes of their products with ambient humidity.

The various types of nylon have generally similar physical properties, being characterized by high toughness, impact strength, and flexibility (Table 4.16). Mechanical properties of nylons are affected significantly by the amount of crystallization in the test piece, ambient temperature (Figure 4.16), and humidity (Figure 4.17), and it is necessary to control these factors carefully in the determination of comparative properties. Moisture has a profound plasticizing influence on the modulus. For example, the Young's modulus values for nylon-6,6 and nylon-6 decreases by about 40% with the absorption of 2% moisture.

Nylons have extremely good abrasion resistance. This property can be further enhanced by addition of external lubricants and by providing a highly crystalline hard surface to the bearings. The surface

TABLE 4.15 Melt Temperatures of Aliphatic Polyamides

Polyamide	T_m (°C)
Nylon-6,6	265
Nylon-6,8	240
Nylon-6,10	225
Nylon-6,12	212
Nylon-6	230
Nylon-7	223
Nylon-11	188
Nylon-12	180

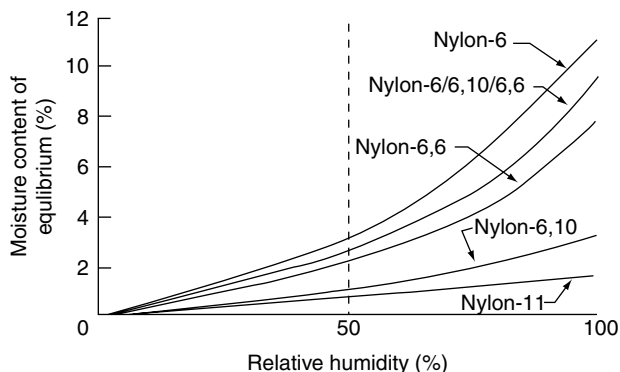


FIGURE 4.14 Effect of relative humidity on the equilibrium moisture absorption of the nylons.

crystallinity can be developed by the use of hot injection molds and by annealing in a nonoxidizing fluid at an elevated temperature (e.g., 150–200°C for nylon-6,6).

The coefficient of friction of nylon-6,6 is lower than mild steel but is higher than the acetal resins. The fractional heat buildup, which determines the upper working limits for bearing applications, is related to the coefficient of friction under working conditions. The upper working limits measured by the maximum LS value (the product of load L in psi on the projected bearing area and the peripheral speed S in ft./min) are 500–1000 for continuous operation of unlubricated nylon-6,6. For intermittent operation initially oiled nylon bearings can be used at LS values of 8000. Higher LS values can be employed with continuously lubricated bearings.

The electrical insulation properties of the nylons are reasonably good at room temperature, under conditions of low humidity, and at low frequencies. Because of the presence of polar amide groups, they are not good insulators for high-frequency work, and since they absorb water, the electrical insulation properties deteriorate as the humidity increases (see Figure 4.18).

The properties of nylons are considerably affected by the amount of crystallization and by the size of morphological structures, such as spherulites, which in turn, are generally influenced by the processing conditions. Thus, a molding of nylon-6, slowly cooled and subsequently annealed, may be 50–60% crystalline, whereas a rapidly cooled thin-walled molding may be only 10% crystalline.

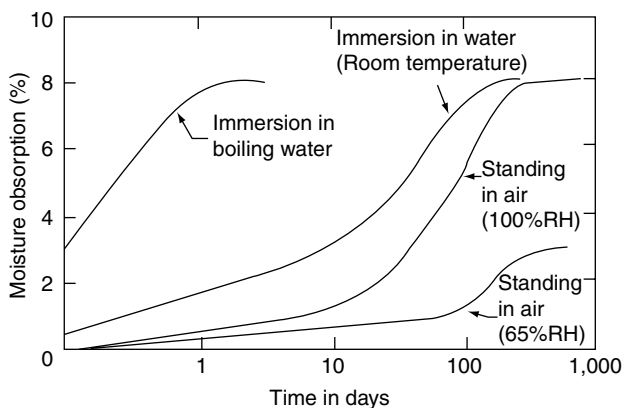


FIGURE 4.15 Effect of environmental conditions on rate of moisture absorption of nylon-6,6 (1/8-in.- thick specimens).

TABLE 4.16 Comparative Properties^a of Typical Commercial Grades of Nylon

Property	6,6	6	6,10	11	12	6,6/6,10/6 (40:30:30)
Specific gravity	1.14	1.13	1.09	1.04	1.02	1.09
Tensile stress at yield 10 ³ lbf/in. ²	11.5	11.0	8.5	5.5	6.6	—
MPa	80	76	55	38	45	—
Elongation at break (%)	80–100	100–200	100–150	300	200	300
Tension modulus 10 ⁵ lbf/in. ²	4.3	4	3	2	2	2
10 ² MPa	30	28	21	14	14	14
Impact strength ft.-lbf/1/2-in. notch	1.0–1.5	1.5–3.0	1.6–2.0	1.8	1.9	—
Rockwell hardness	R118	R112	R111	R108	R107	R83
Heat distortion temperature (264 lbf/in. ²) (°C)	75	60	55	55	51	30
Coefficient of linear expansion 10 ^{−5} cm/cm/°C	10	9.5	15	15	12	—
Volume resistivity ohm-m (dry)	> 10 ¹⁷	> 10 ¹⁷	> 10 ¹⁷	—	—	—
ohm-m (50% RH)	10 ¹⁵	—	10 ¹⁶	—	—	10 ¹⁵
Dielectric constant (10 ³ Hz dry)	3.6–6.0	3.6–6.0	3.6–6.0	—	—	—
Power factor (10 ³ Hz dry)	0.04	0.02–0.06	0.02	—	—	—
Dielectric strength (kV/cm) (25°C, 50% RH)	> 100	> 100	> 100	—	—	—

^a ASTM tests for mechanical and thermal properties.Source: Brydson, J. A. 1982. *Plastic Materials*, Butterworth Scientific, London, UK.

Slowly cooled melts may form bigger spherulites, but rapidly cooled surface layers may be quite different from that of the more slowly cooled centers. The use of nucleating agents (e.g., about 0.1% of a fine silica) can give smaller spherulites and thus a more uniform structure in an injection molding. Such a product may have greater tensile strength, hardness, and abrasion resistance at the cost of some reduction in impact strength and elongation at break: the higher the degree of crystallinity the less the water absorption, and hence the less will be the effect of humidity on the properties of the polymer.

Nylon molding materials are available in a number of grades which many differ in molecular weight and/or in the nature of additives which may be present. The various types of additives used in nylon can be grouped as heat stabilizers, light stabilizers, lubricants, plasticizers, pigments, nucleating agents, flame retarders, and reinforcing fillers.

Heat stabilizers include copper salts, phosphoric acid esters, mercaptobenzothiazole, mercaptobenzimidazole, and phenyl-β-naphthyl-amine. Among light stabilizers are carbon black and various phenolic materials. Self-lubricating grades of nylon which are of value in some gear and bearing applications incorporate lubricants such as molybdenum disulfide (0.2%) and graphite (1%).

Plasticizers may be added to nylon to lower the melting point and to improve toughness and flexibility particularly at low temperatures. A plasticizer used commercially is a blend of *o*- and *p*-toluene ethyl sulfonamide.

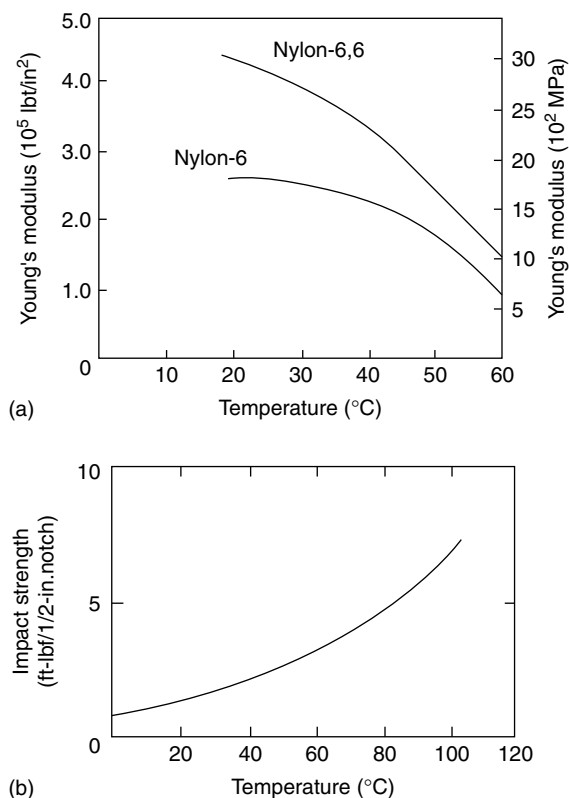


FIGURE 4.16 Effect of temperature on (a) Young's modulus of nylon-6,6 and nylon 6 and (b) impact strength of nylon-6,6.

Substances used as nucleating agents include silica and phosphorus compounds. Nucleating agents are used to control the size of morphological structures of the molding.

There have been substantial efforts to improve the flame resistance of nylons. Various halogen compounds (synergized by zinc oxide or zinc borate) and phosphorus compounds have been used (see the section on [Flame Retardation](#) in [Chapter 1](#)). They are, however, dark in color.

Glass-reinforced nylons have become available in recent years. Two main types of glass fillers used are glass fibers and glass beads. From 20% to 40% glass is used. Compared to unfilled nylons, glass-fiber reinforcement leads to a substantial increase in tensile strength (160 vs. 80 MPa), flexural modulus (8000 vs. 3000 MPa), hardness, creep resistance (at least three times as great), and heat-distortion temperature under load (245 vs. 75°C under 264 psi), and to a significant reduction in coefficient of expansion (2.8×10^{-5} vs. 9.9×10^{-5} cm/cm-°C).

The glass-fiber-filled types can be obtained in two ways. One route involves passing continuous lengths of glass fiber (as rovings) through a polymer melt or solution to produce glass-reinforced nylon strand that is chopped into pellets. Another route involves blending a mixture of resin and glass fibers about 1/4 in. (0.6 cm) long in an extruder. Usually E-grade glass with a diameter of about 0.001 cm treated with a coupling agent, such as a silane, to improve the resin-glass bond is used.

Nylons filled with 4.0% glass spheres have a compressive strength about eightfold higher than unfilled grades, besides showing good improvement in tensile strength, modulus, and heat-distortion temperature. Having low melt viscosity, glass-bead-filled nylons are easier to process than the glass-fiber-filled varieties. They are also more isotropic in their mechanical properties and show minimum warpage. Glass fillers, both fibers and beads, tend to improve self-extinguishing characteristics of nylons.

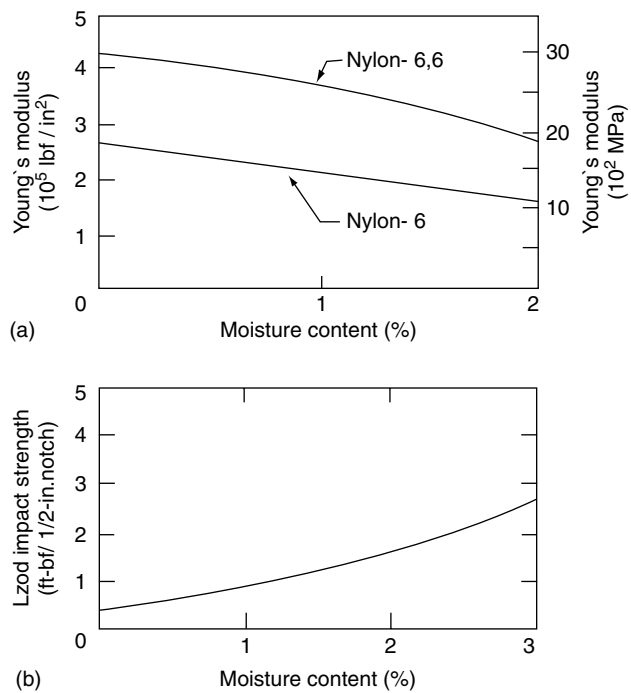


FIGURE 4.17 Effect of moisture content on (a) Young's modulus of nylon-6,6 and nylon-6 and (b) impact strength of nylon-6,6.

4.3.2.1.2 Applications

The most important application of nylons is as fibers, which account for nearly 90% of the world production of all nylons. Virtually all of the rest is used for plastic applications. Because of their high cost, they have not become general-purpose materials, such as polyethylene and polystyrene, which are available at about one-third the price of nylons. Nylons have nevertheless found steadily increasing application as plastics materials for specialty purposes where the combination of toughness, rigidity, abrasion resistance, reasonable heat resistance, and gasoline resistance is important.

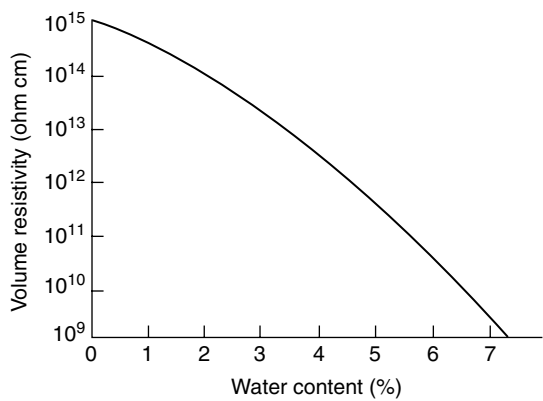


FIGURE 4.18 Effect of moisture content on the volume resistivity of nylon-6,6.

The largest plastics applications of nylons have been in mechanical engineering [14]—nylon-6, nylon-6,6, nylon-6,10, nylon-11, and nylon-12 being mainly used. These applications include gears, cams, bushes, bearings, and valve seats. Zippers made of nylon last longer than traditional ones of fabric or metal. Nylon moving parts have the advantage that they may often be operated without lubrication, and they may often be molded in one piece.

Among the aforesaid nylons, nylon-11 and nylon-12 have the lowest water absorption and are easy to process, but there is some loss in mechanical properties. For the best mechanical properties, the nylon-6,6 would be considered, but this material is also the most difficult to process and has high water absorption. Nylon-6 is easier to process but has even higher water absorption (see [Figure 4.14](#)).

Other applications include sterilizable nylon moldings in medicine and pharmacy, nylon hair combs, and nylon film for packaging foodstuffs (a typical example being milk pouches made of coextruded multilayered films of LDPE/LLDP/nylon-6, with nylon-6 as the barrier layer) and pharmaceutical products. The value of nylon in these latter applications is due to its low odor transmission and the boil-in-the-bag feature. Nylons have reasonable heat resistance. Spatula blades and spoons of nylon-6,6 withstand highest cooking temperatures.

Besides film, other extruded applications of nylons are as monofilaments, which have found applications in surgical sutures, brush tufting, wigs, sports equipment, braiding, outdoor upholstery, and angling.

Production of moldings by polymerization casting of caprolactam and the ability to produce large objects in this way have widened the use of nylon plastics in engineering and other applications. The process gives comparatively stress-free moldings having a reasonably consistent morphological structure with a 45–50% crystallinity, which is higher than melt-processed materials, and thus leads to higher tensile strength, modulus, hardness, and resistance to creep. Products made by polymerization casting include main drive gears for use in the textile and papermaking industries, conveyor buckets used in the mining industry, liners for coal-washing equipment, and propellers for small marine craft.

Glass-filled nylons form the most important group of glass-filled varieties of thermoplastics. Glass-reinforced nylon plastics have high rigidity, excellent creep resistance, low coefficient of friction, high heat-deflection temperature, good low-frequency electrical insulation properties, and they are nonmagnetic in nature. Therefore they have replaced metals in many applications.

Nylons reinforced with glass fibers are thus widely used in domestic appliances, in housings and casing, in car components, including radiator parts, and in the telecommunication field for relay coil formers and tag blocks. Glass-bad-filled nylons have found use in bobbins. Carbon-fiber reinforcement has been used with nylon-6 and nylon-6–nylon-12 mixtures. These materials have found use in the aerospace field and in tennis rackets.

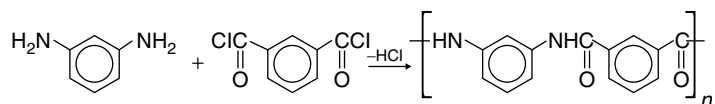
A significant development is the appearance of supertough nylon plastics, which are blends in nylon-6,6 with other resins, such as an ionomer resin used in the initial grades or a modified ethylene–propylene–diene terpolymer rubber (EPDM rubber) used in later grades.

Nylon has been blended with PPO (Vydyne, Noryl GTX), PC, HDPE (Selar), PP, SAN, ABS (Triax, Elemid), PBT (Bexloy), and polyarylates (Bexlar). These blends have lower water absorption than nylon-6,6. Nylon-SAN, which has a high impact strength of 16 ft.-lb/in. of notch (854 J/m), has received a UL (Underwriters Laboratory) rating of 104°C. The nylon-arylate blend is transparent and has a heat-distortion temperature under load (264 lbf/in.²) value of 154°C.

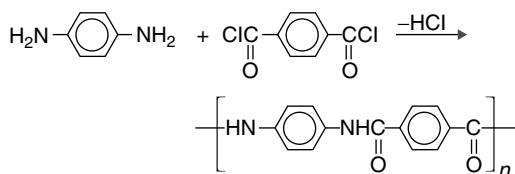
Interest has been aroused by the appearance of novel elastomeric polyamides. The products introduced by Huls under the designation XR3808 and X4006 may be considered as the polyether-amide analogue of the polyether-ester thermoplastic elastomers introduced in the 1970s by Du Pont as Hytrel (see [Figure 4.10](#)). The polyether-amide is a block copolymer prepared by the condensation of polytetramethylene ether glycol (i.e., polytetrahydrofuran) with laurin lactam and decane-1,10-dicarboxylic acid. The elastomeric polyamide XR3808 is reported to have a specific gravity of 1.02, yield stress of 24 MPa, a modulus of elasticity of 300 MPa, and an elongation at break of 360%.

4.3.2.2 Aromatic Polyamides

Aromatic polyamide fibers, better known as aramid fibers, have been defined as “a long chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings [42].” The first significant material of this type was introduced in 1961 by Du Pont as Nomex. It is poly(*m*-phenyleneisophthalamide), prepared from *m*-phenylenediamine and isophthaloyl chloride by interfacial polycondensation.



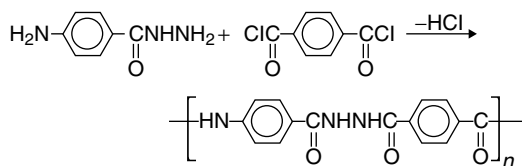
The fiber may be spun from a solution of the polymer in dimethylformamide containing lithium chloride. In 1973, Du Pont commenced production of another aromatic polyamide fiber, a poly(*p*-phenylene terephthalamide) marketed as Kevlar. It is produced by the reaction of *p*-phenylenediamine with terephthaloyl chloride in a mixture of hexamethylphosphoramide and *N*-methyl pyrrolidone (2:1) at -10°C .



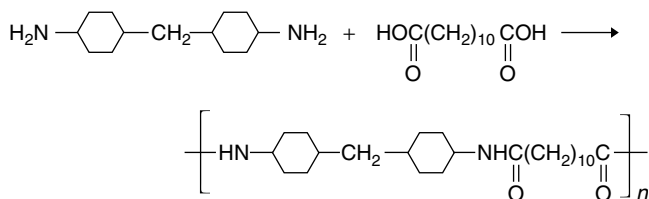
Kevlar fibers are as strong as steel but have one-fifth the weight. Kevlar is thus ideally suited as tire cord materials and for ballistic vests. The fibers have a high T_g ($>300^\circ\text{C}$) and can be heated without decomposition to temperatures exceeding 500°C .

The dimensional stability of Kevlar is outstanding: It shows essentially no creep or shrinkage as high as 200°C . In view of the high melting temperatures of the aromatic polyamides and their poor solubility in conventional solvents, special techniques are required to produce the fibers. For example, Kevlar is wet spun from a solution in concentrated sulfuric acid.

Similar fiber-forming materials have been made available by Monsanto. Thus the product marketed as PABH-T X-500 is made by reacting *p*-aminobenzhydrazide with terephthaloyl chloride.



Polymers have also been prepared from cyclic amines such as piperazine and bis(*p*-aminocyclohexyl)methane. The latter amine is condensed with decanedioic acid to produce the silklike fiber Qiana (Du Pont).

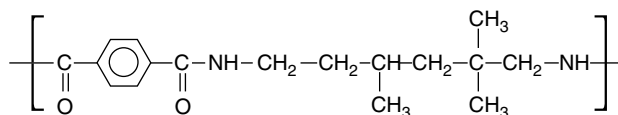


Qiana fibers have a high glass transition temperature (135°C, as compared to 90°C for nylon-6,6), which assures that the polymer will remain in the glassy state during fabric laundering and resist wrinkles and creases.

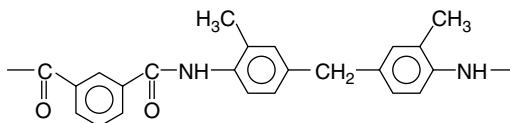
Synthetic fibers range in properties from low-modulus, high-elongation fibers like Lycra (see Section 4.11) to high-modulus high-tenacity fibers such as Kevlar. A breakthrough in fiber strength and stiffness has been achieved with Kevlar. Another high-performance fiber in commercial application is graphite. The use of these new fibers has resulted in the development of superior composite materials, generally referred to as fiber-reinforced plastics or FRPs (see Chapter 2 and Chapter 3), which have shown promise as metal-replacement materials by virtue of their low density, high specific strength (strength/density), and high specific modulus (modulus/density).

Today a host of these FRP products are commercially available as tennis rackets, golf clubs shaft, skis, ship masts, and fishing rods, which are filament wound with graphite and Kevlar fibers. Significant quantities of graphite composites and graphite/Kevlar hybrid composites are used in boeing 757 and 767 planes, which make possible dramatic weight saving. Boron, alumina, and silicon carbide fibers are also high-performance fibers but they are too expensive for large-scale commercial applications.

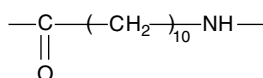
Partially aromatic, melt processable, polyamides are produced as random copolymers, which do not crystallize and are therefore transparent, but are still capable of high-temperature use because of their high T_g values. Several commercial polymers of this type that have glass-like clarity, high softening point, and oil and solvent resistance have been developed. For example, Trogamid T (Dynamit Nobel) contains repeat units of



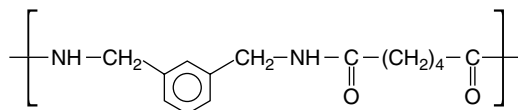
and of 2,4,4-trimethyl isomer, and has a T_g of about 150°C. Grilamid TR (Emser) with a T_g of about 160°C is a copolymer with units of



and of



A crystalline, partially aromatic polyamide, poly-*m*-xylylene-adipamide, (also known as MXD-6) with repeat units of



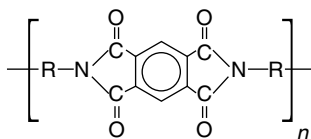
is available as a heat resistant engineering plastic (e.g., Ixef by Solvay) generally similar in properties to nylon-6,6, having a T_m of 243°C but with reduced water absorption, greater stiffness, and a T_g of about 90°C. Although its heat distortion temperature is only 96°C, with 30% glass filling this is increased to about 270°C. Typical properties of some of these polyamides, along with those of nylon-6,6 for comparison, are shown in Table 4.17.

Copolymers containing amide and imide units, the polyamideimides, are described in the following section on polyimides.

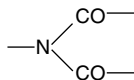
TABLE 4.17 Properties of Polyamides

Property	Nylon-6,6	Ixef(High-Impact Grade)	Trogamid T	Nomex (Fiber)	Kevlar
Tensile strength					
10 ³ lbf/in. ²	9.4	25.7	8.7	97.2	435
MPa	65	177	60	670	3000
Tensile modulus					
10 ⁵ lbf/in. ²	4.6	19.4	4.4	25.5	194
GPa	3.2	13.4	3.0	17.6	134
Elongation at break (%)	100	2.7	132	22	2.6
Flexural modulus					
10 ⁵ lbf/in. ²	4.8	14.8	—	—	—
GPa	3.3	10.2	—	—	—
Impact strength, notched Izod					
ft.-lb/in.	1.3	3.0	—	—	—
J/m	69	159	—	—	—

4.3.2.3 Polyimides



The polyimides have the characteristic functional group



and are thus closely related to amides [43]. The branched nature of the imide functional group enables production of polymers having predominantly ring structures in the backbone and hence high softening points. Many of the structures exhibit such a high level of thermal stability that they have become important for application at much higher service temperatures than had been hitherto achieved with polymer.

The use of tetracarboxylic acid anhydride instead of the dicarboxylic acids used in the manufacture of polyamides yields polyimides. The general method of preparation of the original polyimides by the polymerization of pyromellitic dianhydride and aromatic diamine is shown in [Figure 4.18a](#). A number of diamines have been investigated, and it has been found that certain aromatic amines, which include *m*-phenylenediamine, benzidine, and di-(4-aminophenyl)ether, give polymers with a high degree of oxidative and thermal stability.

The aromatic amine di(4-aminophenyl)ether is employed in the manufacture of polyimide film, designated as Kapton (Du Pont). Other commercial materials of this type introduced by Du Pont in the early 1960s included a coating resin (Pyre ML) and a machinable block form (Vespel). In spite of their high price these materials have found established uses because of their exceptional heat resistance and good retention of properties at high temperatures.

Since the polyimides are insoluble and infusible, they are manufactured in two stages. The first stage involves an amidation reaction carried out in a polar solvent (such as dimethylformamide and dimethylacetamide) to produce an intermediate poly(amic acid) which is still soluble and fusible. The

poly(amic acid) is shaped into the desired physical form of the final product (e.g., film, fiber, coating, laminate) and then the second stage of the reaction is carried out.

In the second stage the poly(amic acid) is cyclized in the solid state to the polyimide by heating at moderately high temperatures above 150°C. A different approach, avoiding the intermediate poly(amic acid) step, was pioneered by Upjohn. The Upjohn process involves the self-condensation of the isocyanate of trimellitic acid, and the reaction by-product is carbon dioxide (Figure 4.19b).

Polypyromellitimides (Figure 4.19a) have many outstanding properties: flame resistance, excellent electrical properties, outstanding abrasion resistance, exceptional heat resistance, and excellent resistance to oxidative degradation, most chemicals (except strong bases), and high-energy radiation. After 1000 h of exposure to air at 300°C the polymers retained 90% of their tensile strength, and after 1500 h exposure to a radiation of about 10 rad at 175°C, they retained form stability, although they became brittle.

The first commercial applications of polypyromellitimides were as wire enamels, as insulating varnishes, as coating for glass cloth (Pyre ML, Du Pont), and as film (Kapton, Du Pont). A fabricated solid grade was marketed as Vespel (Du Pont). Laminates were produced by impregnation of glass and carbon fiber, with the polyimide precursor followed by pressing and curing at about 200°C and further curing at temperatures of up to 350°C. Such laminates could be used continuously at temperatures up to 250°C and intermittently to 400°C. The laminates have thus found important application in the aircraft industry, particularly in connection with supersonic aircraft.

At the present time the applications of polyimides include compressor seals in jet engines, sleeves, bearings, pressure discs, sliding and guide rolls, and friction elements in data processing equipment, valve shafts in shutoff valves, and parts in soldering and welding equipment.

Polyimides have also found a number of specialist applications. Polyimide foams (Skybond by Monsanto) have been used for sound deadening of jet engines. Polyimides fibers have been produced by Upjohn and by Rhone-Poulenc (Kermel).

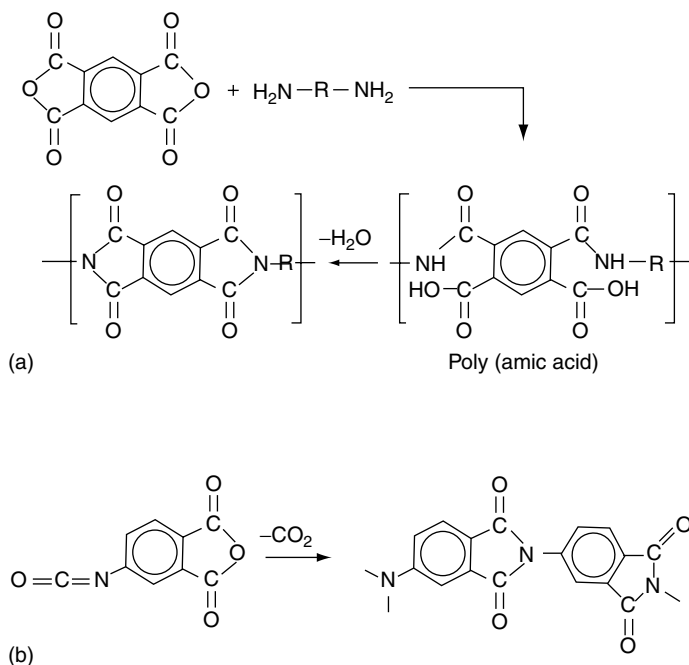


FIGURE 4.19 (a) Synthesis of polyimides by polycondensation. (b) Self-condensation of isocyanate of trimellitic acid.

A particular drawback of the polyimides is that they have limited resistance to hydrolysis and may crack in water or steam at temperatures above 100°C. Consequently, polyimides have encountered competition from polyetheretherketones (PEEK), which are not only superior in this regard but are also easier to mold.

4.3.2.3.1 Modified Polyimides

The application potential of polyimides is quite limited because, being infusible, they cannot be molded by conventional thermoplastics techniques [14]. In trying to overcome this limitation, scientists, in the early 1970s, developed commercially modified polyimides, which are more tractable materials than polyimides but still possessing significant heat resistance. The important groups of such modified polyimides are the polyamideimides (e.g., Torlon by Amoco Chemicals), the polybismaleinimides (e.g., Kinel by Rhone-Poulenc), the polyester-imides (e.g., Icdal Ti40 by Dynamit Nobel), and the polyether-imides (e.g., Ultem by General Electric).

If trimellitic anhydride is used instead of pyromellitic dianhydride in the reaction shown in Figure 4.19a, then polyamide-imide is formed (see Figure 4.20a). Other possible routes to this type of product involve the reaction of trimellitic anhydride with diisocyanates, (Figure 4.20b) or diurethanes (Figure 4.20c). Closely related is the Upjohn process for polyimide by self-condensation of the isocyanate of trimellitic acid, as illustrated in Figure 4.19b, although the product in this case is a true polyimide rather than a polyamide-imide.

Polyamide-imides may also be produced by reacting together pyromellitic dianhydride, a diamine, and a diacid chloride. Alternatively, it may be produced in a two-stage process in which a diacid chloride is reacted with an excess of diamine to produce a low-molecular-weight polyamide with amine end

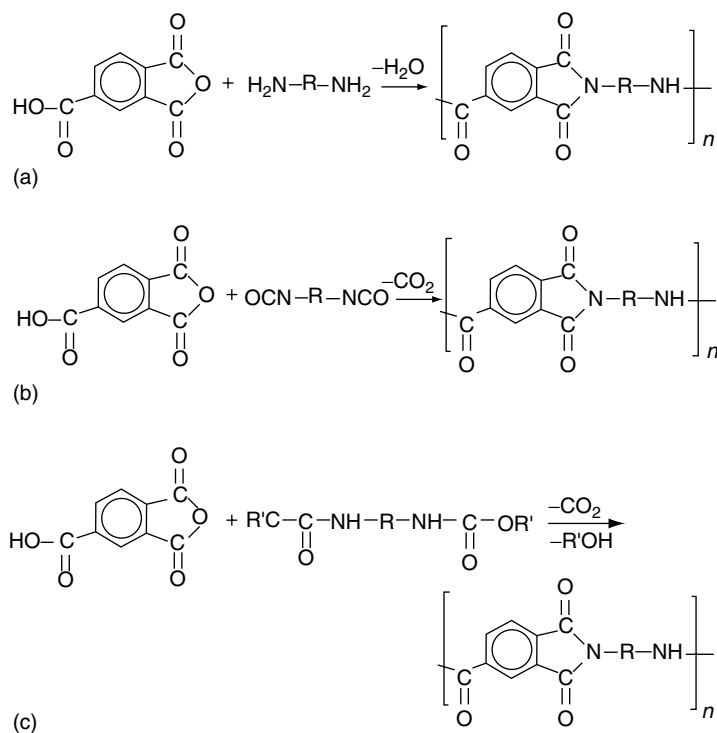


FIGURE 4.20 Synthesis of polyamide-imides from trimellitic anhydride and (a) diamine, (b) diisocyanate, and (c) diurethane.

groups which may then be chain extended by reaction with pyromellitic dianhydride to produce imide linkages.

The Torlon materials produced by Amoco Chemicals are polyamide-imides of the type shown in Figure 4.20a. Torlon has high strength, stiffness, and creep resistance, shows good performance at moderately high temperatures, and has excellent resistance to radiation. The polymers are unaffected by all types of hydrocarbons (including chlorinated and fluorinated products), aldehydes, ketones, ethers, esters, and dilute acids, but resistance to alkalis is poor.

Torlon has been marketed both as a compression-molding grade and as an injection-molding grade. The compression-molding grade, Torlon 2000, can accept high proportions of filler without seriously affecting many of its properties. For compression molding, the molding compound is preheated at 280°C before it is molded at 340°C at pressures of 4350 psi (30 MPa); the mold is cooled at 260°C before removal.

For injection molding, the melt at temperatures of about 355°C is injected into a mold kept at about 230°C. To obtain high-quality moldings, prolonged annealing cycles are recommended.

Uses of polyamide-imides include pumps, valves, refrigeration plant accessories, and electronic components. The polymers have low coefficient of friction, e.g., 0.2 (to steel), which is further reduced to as little as 0.02–0.08 by blending with graphite and Teflon. In solution form in *N*-methyl-2-pyrrolidone, Torlon has been used as a wire enamel, as a decorative finish for kitchen equipment, and as an adhesive and laminating resin in spacecraft.

The polyimides and polyamide-imides are produced by condensation reactions which give off volatile low-molecular-weight by-products. The polybismaleinimides may however be produced by rearrangement polymerization with no formation of by-products. The starting materials in this case are the bismaleimides, which are synthesized by the reaction of maleic anhydride with diamines (Figure 4.21).

The bismaleimides can be reacted with a variety of bifunctional compounds to form polymers by rearrangement reactions. These include amines, mercaptans, and aldoximes (Figure 4.22). If the reaction is carried out with a deficiency of the bifunctional compound, the polymer will have terminal double bonds to serve as a cure site for the formation of a cross-linked polymer via a double bond polymerization mechanism during molding. The cross-linked in this case occurs without the formation of any volatile by-products.

The Kinel materials produced by Rhone-Poulenc are polybismaleinimides of the type shown in Figure 4.22. These materials have chain-end double bonds, as explained previously, can be processed like conventional thermosetting plastics. The properties of the cured polymers are broadly similar to the polyimides and polyamide-imides. Molding temperatures are usually from 200°C to 260°C. Post-curing at 250°C for about 8 h is necessary to obtain the optimum mechanical properties.

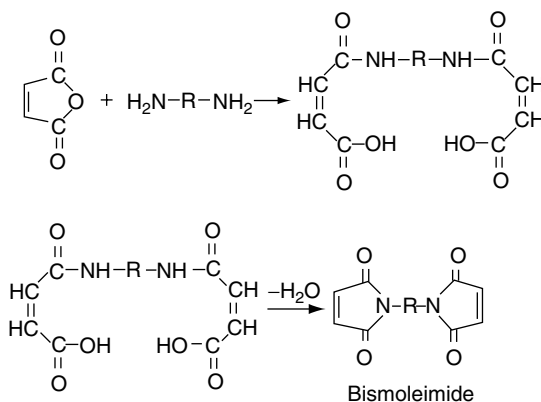


FIGURE 4.21 Synthesis of bismaleimides by the reaction of maleic anhydride with diamines.

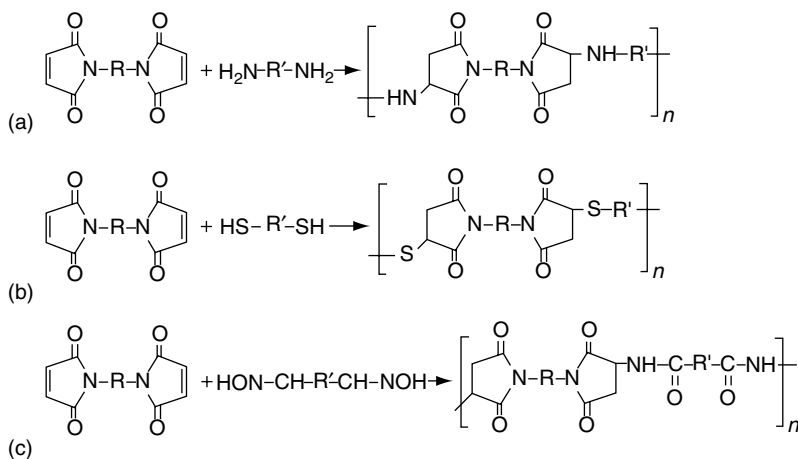
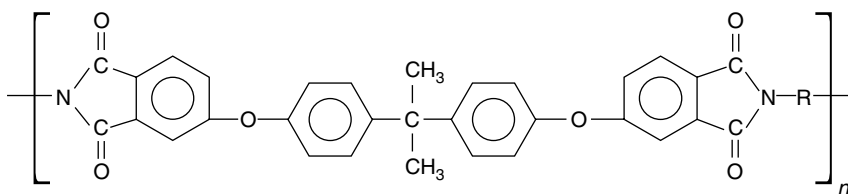


FIGURE 4.22 Formation of polymers by reaction of bismaleimides with (a) amines, (b) mercaptans, and (c) aldoximes.

Polybismaleinimides are used for making laminates with glass- and carbon-fiber fabrics, for making printed circuit boards, and for filament winding. Filled grades of polybismaleinimides are available with a variety of fillers such as asbestos, glass fiber, carbon fiber, graphite, Teflon, and molybdenum sulfide. They find application in aircraft, spacecraft, and rocket and weapons technology. Specific uses include fabrication of rings, gear wheels, friction bearings, cam discs, and brake equipment.

The polyester-imides constitute a class of modified polyimide. These are typified by the structure shown in Figure 4.23. Polyether-imides form yet another class of modified polyimide. These are high-performance amorphous thermoplastics based on regular repeating ether and imide linkages. The aromatic imide units provide stiffness, while the ether linkages allow for good melt-flow characteristics and processability.

One of several synthetic routes to polyetherimides of a general structure involves a cyclization reaction of form the imide rings and a displacement reaction to prepare the ether linkages and form the polymer



The first step of this synthesis is to form a bis-imide monomer formed by the reaction of nitrophthalic anhydride and a diamine (see Figure 4.21). The second step of polyetherimide synthesis involves the formation of a bisphenol dianion by treatment of a diphenol with two equivalents of base, followed by

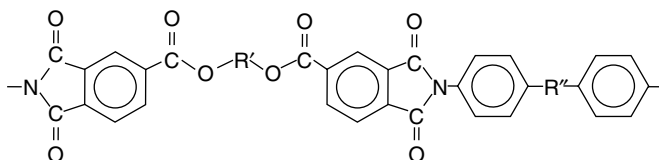


FIGURE 4.23 Typical structure of polyester-imides.

removal of water. The polymerization step involves displacement of the nitrogroups of the bis-imide by the bisphenol dianion to form the ether linkages of the polymer. A large number of polyetherimides can be prepared by the synthetic route.

Polyetherimides are suitable for applications that require high temperature stability, high mechanical strength, inherent flame resistance with extremely low smoke evolution, outstanding electrical properties over a wide frequency and temperature range, chemical resistance to aliphatic hydrocarbons, acids and dilute bases, UV stability, and ready processability on conventional equipment.

Ultem, introduced by General Electric in 1982, is a polyether-imide. It was designed to compete with heat- and flame-resistive, high-performance engineering polymers, polysulfones, and polyphenylene sulfide. Some typical properties of Ultem 1000 are specific gravity 1.27, tensile yield strength 105 MPa, flexural modulus 3300 MPa, hardness Rockwell M109, Vicat softening point 219°C, heat-distortion temperature (1.82 MPa) 200°C, and limiting oxygen index 47. Specific applications include circuit breaker housings and microwave oven stirrer shafts.

Typical properties of unfilled polyimides are compared in Table 4.18.

4.3.3 Formaldehyde Resins

The phenol-formaldehyde and urea-formaldehyde resins are the most widely used thermoset polymers. The phenolic resins were the first truly synthetic polymers to be produced commercially. Both phenolic and urea resins are used in the highly cross-linked final form (C-stage), which is obtained by a stepwise polymerization process. Lower-molecular-weight prepolymers are used as precursors (A-stage resins), and the final form and shape are generated under heat and pressure. In this process water is generated in the form of steam because of the high processing temperatures. Fillers are usually added to reduced resin content and to improve physical properties. The preferred form of processing is compression molding.

The phenolics and urea resins are high-volume thermosets which owe their existence to the relatively low cost of the starting materials and their superior thermal and chemical resistance. Today these resins are widely used in molding applications, in surface coatings and adhesives, as laminating resins, casting resins, binders and impregnants, and in numerous other applications. However, as with all products based on formaldehyde, there is concern about the toxicity of these resins during processing and about the residual traces of formaldehyde in the finished product.

TABLE 4.18 Properties of Unfilled Polyimides

Property	Vespel (ICI)	Torlon (Amoco)	Kinel (Rhône-Poulenc)	Ultem (General Electric)
Tensile strength (MPa)				
25°C	90	186	~ 40	100
150°C	67	105	—	—
260°C	58	52	~ 25	—
Flexural modulus (GPa)				
25°C	3.5	4.6	3.8	3.3
150°C	2.7	3.6	—	2.5
260°C	2.3	3.0	2.8	—
Heat distortion temperature (°C)	357	282	—	200
Limiting oxygen index (%)	35	42	—	47

4.3.3.1 Phenol–Formaldehyde Resins

Monomers	Polymerization	Major Uses
Phenol, formaldehyde	Base- or acid-catalyzed stepwise polycondensation	Plywood adhesives (34%), glass-fiber insulation (19%), molding compound (8%)

Since the cross-linked polymer of phenol-formaldehyde reaction is insoluble and infusible, it is necessary for commercial applications to produce first a tractable and fusible low-molecular-weight prepolymer which may, when desired, be transformed into the cross-linked polymer [14,44,45]. The initial phenol-formaldehyde products (prepolymers) may be of two types: *resols* and *novolacs*.

4.3.3.1.1 Resols

Resols are produced by reacting a phenol with a molar excess of formaldehyde (commonly about 1:1.5–2) by using a basic catalyst (ammonia or sodium hydroxide). This procedure corresponds to Baekeland's original technique. Typically, reaction is carried out batchwise in a resin kettle equipped with stirrer and jacketed for heating and cooling. The resin kettle is also fitted with a condenser such that either reflux or distillation may take place as required.

A mixture of phenol, formalin, and ammonia (1–3% on the weight of phenol) is heated under reflux at about 100°C for 0.25–1 h, and then the water formed is removed by distillation, usually under reduced pressure to prevent heat hardening of the resin.

Two classes of resins are generally distinguished. Resols prepared with ammonia as catalysts are spirit-soluble resins having good electrical insulation properties. Water-soluble resols are prepared with caustic soda as catalyst. In aqueous solutions (with a solids content of about 70%) these are used mainly for mechanical grade paper and cloth laminates and in decorative laminates.

The reaction of phenol and formaldehyde in alkaline conditions results in the formation of *o*- and *p*-methylol phenols. These are more reactive towards formaldehyde than the original phenol and undergo rapid substitution with the formation of di- and trimethylol derivatives. The methylol phenols obtained are relatively stable in an alkaline medium but can undergo self-condensation to form dinuclear and polynuclear phenols (of low molecular weight) in which the phenolic nuclei are bridged by methylene groups. Thus in the base-catalyzed condensation of phenol and formaldehyde, there is a tendency for polynuclear phenols, as well as mono-, di-, and trimethylol phenols to be formed.

Liquid resols have an average of less than two phenolic nuclei per molecule, and a solid resol may have only three or four. Because of the presence of methylol groups, the resol has some degree of water tolerance. However, for the same reason, the shelf life of resols is limited.

Resols are generally neutralized or made slightly acidic before cure (cross-linking) is carried out. Network polymers are then obtained simply by heating, which results in cross-linking via the uncondensed methylol groups or by more complex mechanisms (see Figure 4.24). Above 160°C it is believed that quinone methide groups, as depicted on the bottom of Figure 4.24, are formed by condensation of the ether linkages with the phenolic hydroxyl groups. These quinone methide structures can be cross-linked by cycloaddition and can undergo other chemical reactions. It is likely that this formation of quinone methide and other related structures is responsible for the dark color of phenolic compression moldings made at higher temperatures. Note that cast phenol-formaldehyde resins, which are cured at much lower temperatures, are water white in color. If they are heated to about 180°C, they darken considerably.

4.3.3.1.2 Novolac

The resols we have described are sometimes referred to as *one-stage resins*, since cross-linked products may be made from the initial reaction mixture only by adjusting the pH. The resol process is also known as the *one-stage* process. On the other hand, the novolacs are sometimes referred to as *two-stage* resins because, in this case, it is necessary to add, as we will show, some agent to enable formation of cross-linked products.

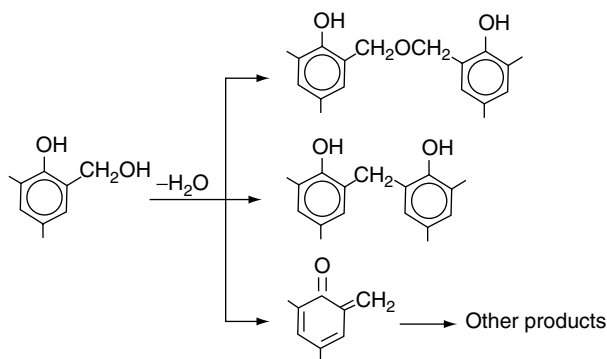


FIGURE 4.24 Curing mechanisms for resols.

Novolac resins are normally prepared by the reaction of a molar excess of phenol with formaldehyde (commonly about 1.25:1) under acidic conditions. The reaction is commonly carried out batchwise in a resin kettle of the type used for resol manufacture. Typically, a mixture of phenol, formalin, and acid is heated under reflux at about 100°C. The acid is usually either hydrochloric acid (0.1–0.3% on the weight of phenol) or oxalic acid (0.5–2%).

Under acidic conditions the formation of methylol phenols is rather slow, and the condensation reaction thus takes approximately 2–4 h. When the resin reaches the requisite degree of condensation, it become hydrophobic, and the mixture appears turbid. Water is then distilled off until a cooled sample of the residual resin shows a melting point of 65–75°C. The resin is then discharged and cooled to give a hard, brittle solid (*novolac*).

Unlike resols, the distillation of water for *novolac* is normally carried out without using a vacuum. Therefore the temperature of the resin increases as the water is removed and the reaction proceeds, the temperature reaching as high as 160°C at the end. At these temperatures the resin is less viscous and more easily stirred.

The mechanism and phenol-formaldehyde reaction under acidic conditions is different from that under basic conditions described previously. In the presence of acid the products *o*- and *p*-methylol phenols, which are formed initially, react rapidly with free phenol to form dihydroxy diphenyl methanes (Figure 4.25). The latter undergo slow reaction with formaldehyde and phenolic species, forming polynuclear phenols by further methylolation and methylol link formation. Reactions of this type continue until all the formaldehyde has been used up. The final product thus consists of a complex mixture of polynuclear phenols linked by *o*- and *p*-methylene groups.

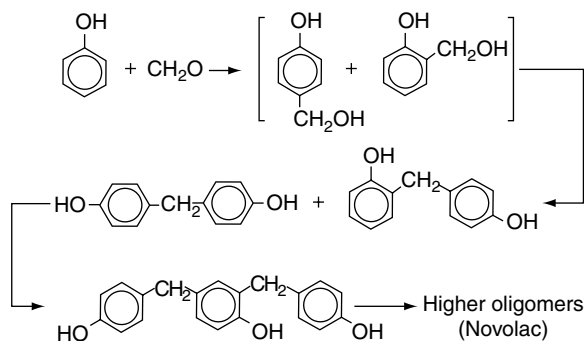


FIGURE 4.25 Formation of novolac in an acid-catalyzed reaction of phenol and formaldehyde.

The average molecular weight of the final product (novolac) is governed by the initial molar ratio of phenol and formaldehyde. A typical value of average molecular weight is 600, which corresponds to about six phenolic nuclei per chain. The number of nuclei in individual chains is usually 2–13.

A significant feature of novolacs is that they represent completed reactions and as such have no ability to continue increasing in average molecular weight. Thus there is no danger of gelation (cross-linking) during novolac production. Resols, however, contain reactive methylol groups and so are capable of cross-linking on heating.

To convert novolacs into network polymers, the addition of a cross-linking agent (hardener) is necessary. Hexamethylenetetramine (also known as hexa or hexamine) is invariably used as the hardener. The mechanism of the curing process is complex.

Because of the exothermic reaction on curing and the accompanying shrinkage, it is necessary to incorporate inert fillers to reduce resin content. Fillers also serve to reduce cost and may give additional benefits, such as improving the shock resistance. Commonly used fillers are wood flour, cotton flock, textile shreds, mica, and asbestos.

Wood flour, a fine sawdust preferably from soft woods, is the most commonly used filler. Good adhesion occurs between the resin and the wood flour, and some chemical bonding may also occur. Wood flour reduces exotherm and shrinkage, improves the impact strength of the moldings, and is cheap. For better impact strength cotton fabric or chopped fabric may be incorporated. Asbestos may be used for improved heat and chemical resistance, and iron-free mica powder may be used for superior electrical insulation resistance characteristics.

Other ingredients which may be incorporated into a phenolic molding powder include *accelerators* (e.g., lime or magnesium oxide) to promote the curing reaction, *lubricants* (e.g., stearic acid and metal stearates) to prevent sticking to molds, *plasticizers* (e.g., naphthalene, furfural, and dibutyl phthalate) to improve flow properties during cure, and *pigments* or *dyes* (e.g., nigrosine) to color the product. Some typical formulations of phenolic molding powders are given in Table 4.19.

Since the phenolic resins cure with evolution of volatiles, compression molding is performed using molding pressures of 1–2 tn/in.² (15–30 MPa) at 155–170°C. Phenolic molding compositions may be preheated by high frequency or other methods. Preheating reduces cure time, shrinkage, and required molding pressures. It also enhances the ease of flow, with consequent reduction of mold wear and danger of damage to inserts. Molding shrinkage of general-purpose grades is about 0.005–0.08 in./in. Highly loaded mineral-filled grades exhibit lower shrinkage.

Phenol–formaldehyde molding compositions are traditionally processed on compression- and transfer-molding machines with a very small amount being extruded. However, the injection-molding process as modified for thermosetting plastics is being increasingly used and it is today the most common method used to process phenolic compounds. The shorter cycle times and low waste factor available with

TABLE 4.19 Typical Formulations^a of Phenolic Molding Grades

Ingredient	General-Purpose Grade	Medium Shock-Resisting Grade	High Shock-Resisting Grade	Electrical Grade
Novolac resin	100	100	100	100
Hexa	12.5	12.5	17	14
Magnesium oxide	3	2	2	2
Magnesium stearate	2	2	3.3	2
Nigrosine dye	4	3	3	3
Wood Flour	100	—	—	—
Cotton flock	—	110	—	—
Textile shreds	—	—	150	—
Asbestos	—	—	—	40
Mica	—	—	—	120

^a Parts by weight.

Source: Brydson, J. A. 1982. *Plastic Materials*, Butterworth Scientific, London, UK.

screw injection molding, which contribute to the lowest unit costs for extended runs, have induced phenolic molding compounders to develop products for this molding process.

4.3.3.1.3 *Properties and Applications*

Since the polymer in phenolic moldings is highly cross-linked and interlocked, the moldings are hard, infusible, and insoluble. The chemical resistance of the moldings depends on the type of resin and filler used. General-purpose PF grades are readily attacked by aqueous sodium hydroxide, but cresol- and xylenol-based resins are more resistant. Phenolic moldings are resistant to acids except formic acid, 50% sulfuric acid, and oxidizing acids. The resins are ordinarily stable up to 200°C.

The mechanical properties of phenolic moldings are strongly dependent on the type of filler used (Table 4.20). Being polar, the electrical insulation properties of phenolics are not outstanding but are generally adequate. A disadvantage of phenolics as compared to aminoplasts and alkyds is their poor tracking resistance under high humidity, but this problem is not serious, as will be evident from the wide use of phenolics for electrical insulation applications.

Perhaps the most well-known applications of PF molding compositions are in domestic plugs and switches. However, in these applications PF has now been largely replaced by urea-formaldehyde plastics because of their better antitracking property and wider range of color possibility. (Because of the dark color of the phenolic resins molded above 160°C, the range of pigments available is limited to relatively darker colors—blacks, browns, deep blues, greens, reds, and oranges.) Nevertheless, phenolics continue to be used as insulators in many applications because their properties have proved quite adequate.

There are also many applications of phenolics where high electrical insulation properties are not as important, and their heat resistance, adequate shock resistance, and low cost are important features: for example, knobs, handles, telephones, and instrument cases. In some of these applications phenolics have been replaced by ureaformaldehyde, melamine-formaldehyde, alkyd, or newer thermoplastics because of the need for brighter colors and tougher products.

In general, phenolics have better heat and moisture resistance than ureaformaldehyde moldings. Heat-resistant phenolics are used in handles and knobs of cookware, welding tongs, electric iron parts, and in the automobile industry for fuse box covers, distributor heads, and other applications where good electrical insulation together with good heat resistance is required.

Bottle caps and closures continue to be made in large quantities from phenolics. The development of machines for injection molding of thermosetting plastics and availability of fast-curing grades of phenolics have stimulated the use of PF for many small applications in spite of competition from other plastics.

Among the large range of laminated plastics available today, the phenolics were the first to achieve commercial significance, and they are still of considerable importance. In these applications one-stage resins (resols) are used, since they have sufficient methylol groups to enable curing without the need of a curing agent.

Caustic soda is commonly used as the catalyst for the manufacture of resols for mechanical and decorative laminates. However, it is not used in electrical laminates because it adversely affects the electrical insulation properties. For electrical-grade resols ammonia is the usual catalyst, and the resins are usually dissolved in industrial methylated spirits. The use of cresylic acid (*m*-cresol content 50–55%) in place of phenol yields laminating resins of better electrical properties.

In the manufacture of laminates for electrical insulation, paper (which is the best dielectric) is normally used as the base reinforcement. Phenolic paper laminates are extensively used for high-voltage insulation applications.

Besides their good insulation properties, phenolic laminates also possess good strength, high rigidity, and machinability. Sheet, tubular, and molded laminates are employed. Phenolic laminates with cotton fabric reinforcement are used to manufacture gear wheels that run quietly but must be used at lower working stresses than steel. Phenolic-cotton or phenolic-asbestos laminates have been used as bearings for steel rolling mills to sustain bearing loads as high as 3000 psi (21 MPa). Because of the advent of

TABLE 4.20 Properties of Phenolic Moldings

Property	General-Purpose Grade	Medium Shock-Resisting Grade	High Shock-Resisting Grade	Electrical Grade
Specific gravity	1.35	1.37	40	1.85
Shrinkage (cm/cm)	0.006	0.005	0.002	0.002
Tensile strength				
lbf/in. ²	8000	7000	6500	8500
MPa	55	48	45	58
Impact strength				
ft.-lbf	0.16	0.29	0.8–1.4	0.14
J	0.22	0.39	1.08–1.9	0.18
Dielectric constant				
at 800 Hz	6.0–10.0	5.5–5.7	6.0–10.0	4.0–6.0
at 10 ⁶ Hz	4.5–5.5	—	—	4.3–5.4
Dielectric strength				
(20°C)				
V/mil	150–300	200–275	150–250	275–350
kV/cm	58–116	78–106	58–97	106–135
Power factor				
at 800 Hz	0.1–0.4	0.1–0.35	0.1–0.5	0.03–0.05
at 10 ⁶ Hz	0.03–0.05	—	—	0.01–0.02
Volume resistivity	10 ¹² –10 ¹⁴	10 ¹² –10 ¹⁴	10 ¹¹ –10 ¹³	10 ¹³ –10 ¹⁶
(ohm-m)				
Water absorption				
(24 h, 23°C)				
mg	45–65	30–50	50–100	2–6

^a Testing according to BS 2782.

Source: Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.

cheaper thermoplastics, cast phenolic resins (resols) are no longer an important class of plastics materials.

4.3.3.2 Urea–Formaldehyde Resins

Monomers	Polymerization	Major Uses
Urea, formaldehyde	Stepwise polycondensation	Particle-board binder resin (60%), paper and textile treatment (10%), molding compound (9%) coatings (7%)

Aminoresins or *aminoplastics* cover a range of resinous polymers produced by reaction of amines or amides with aldehydes [14,46,47]. Two such polymers of commercial importance in the field of plastics are the urea-formaldehyde and melamine-formaldehyde resins. Formaldehyde reacts with the amino groups to form aminomethylol derivatives which undergo further condensation to form resinous products. In contrast to phenolic resins, products derived from urea and melamine are colorless.

Urea and formaldehyde resins are usually prepared by a two-stage reaction. In the first stage, urea and formaldehyde (mole ratio in the range 1:1.3–1:1.5) are reacted under mildly alkaline (pH 8) conditions, leading to the production of monomethylol urea (Figure 4.26(I)) and dimethylol urea (Figure 4.26(II)). If the product of the first stage, which in practice usually also contains unreacted urea and formaldehyde, is subjected to acid conditions at elevated temperatures (stage 2), the solution increases in viscosity and sets to an insoluble and irreversible gel. The gel eventually converts with evolution of water and formaldehyde to a hard, colorless, transparent, insoluble, and infusible mass having a network molecular structure.

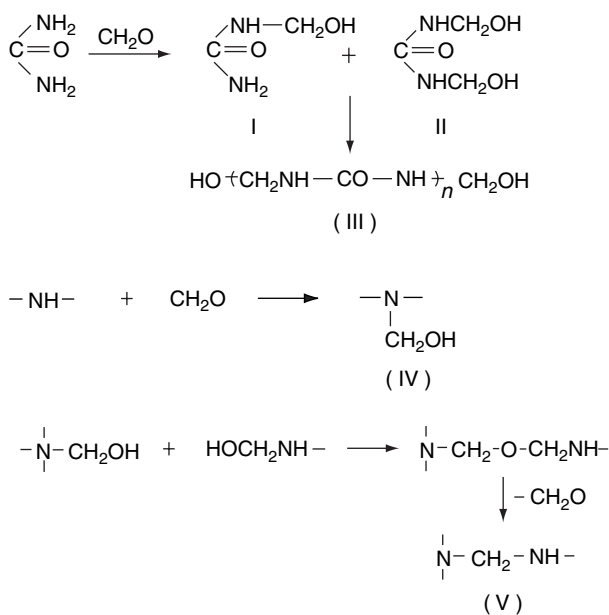


FIGURE 4.26 Reactions in the formation of urea-formaldehyde resins.

The precise mechanisms involved during the second stage are not fully understood. It does appear that in the initial period of the second stage methylol ureas condense with each other by reaction of a $-\text{CH}_2\text{OH}$ group on one molecule with an $-\text{NH}_2$ of another molecule, leading to linear polymers of the form shown in Figure 4.26(III). These polymers are relatively less soluble in aqueous media and tend to form amorphous white precipitates on cooling to room temperature.

More soluble resins are formed on continuation of heating. This probably involves the formation of pendant methylol groups (Figure 4.26(IV)) by reactions of the $-\text{NH}-$ groups with free formaldehyde. These methylol groups and the methylol groups on the chain ends of the initial reaction product can then react with each other to produce ether linkages, or with amine groups to give methylene linkages (Figure 4.26(V)). The ether linkages may also break down on heating to methylene linkages with the evolution of formaldehyde (Figure 4.26(V)). An idealized network structure of the final cross-linked product is shown in Figure 1.25.

4.3.3.2.1 Molding Powder

The urea-formaldehyde (UF) Molding powder will contain a number of ingredients. Most commonly these include resin, filler, pigment, accelerator, stabilizer, lubricant, and plasticizer.

Bleached wood pulp is employed as a filler for the widest range of bright colors and in slightly translucent moldings. Wood flour, which is much cheaper, may also be used.

A wide variety of pigments is now used in UF molding compositions. Their principal requirements are that they should be stable to processing conditions and be unaffected by service conditions of the molding.

To obtain a sufficiently high rate of cure at molding temperatures, it is usual to add about 0.2–2.0% of an accelerator (hardener)—a latent acid catalyst which decomposes at molding temperatures to yield an acidic body that will accelerate the rate of cure. Many such materials have been described, the most prominent of them being ammonium sulfamate, ammonium phenoxylacetate, trimethyl phosphate, and ethylene sulfite. A stabilizer such as hexamine is often incorporated into the molding powder to improve its shelf life.

Metal stearates, such as zinc, magnesium, or aluminum stearates are commonly used as lubricants at about 1% concentration. Plasticizers (e.g., monocresyl glycidyl ether) are used in special grades of

molding powders. They enable more highly condensed resins to be used in the molding powder and thus reduce curing shrinkage while maintaining good flow properties.

In a typical manufacturing process, the freshly prepared UF first-stage reaction product is mixed with the filler (usually with a filler-resin dry weight ratio of 1:2) and other ingredients except pigment in a trough mixer at about 60°C for about 2 h. Thorough impregnation of the filler with the resin solution and further condensation of the resin takes place during this process. Next, the wet mix is in a turbine or rotary drier for about 2 h at 100°C or about 1 h in a countercurrent of air at 120–130°C. The drying process reduces the water content from about 40% to about 6% and also causes further condensation of the resin.

After it is removed from the drier, the product is ground in a hammer mill and then in a ball mill for 6–9 h. The pigments are added during the ball-milling process, which ensures a good dispersion of the pigment and gives a fine powder that will produce moldings of excellent finish. The powder, however, has a high bulk factor and needs densification to avoid problems of air and gas trappings during molding.

There are several methods of densification. In one method, the heated powder is formed into strips by passing through the nip of a two-roll mill. The strips are then powdered into tiny flat flakes in a hammer mill. Other processes involve agglomeration of the powder by heating in an internal mixer at about 100°C or by treatment with water or steam and subsequent drying. Continuous compounders, such as the Buss Ko-Kneader, are also used.

4.3.3.2.2 Processing

Urea–formaldehyde molding powders have a limited storage life. They should therefore be stored in a cool place and should be used, wherever possible, within a few months of manufacture. Conventional compression and transfer molding are commonly used for UF materials, the former being by far the most important process in terms of tonnage handled. Compression molding pressures usually range from 1 to 4 tn/in.² (15–60 MPa), the higher pressures being used for deep-draw articles. Molding temperatures from 125°C to 160°C are employed. The cure time necessary depends on the mold temperature and on the thickness of the molding. The cure time for a 1/8 in. thick molding is typically about 55 sec at 145°C. Bottle caps (less than 1/8 in. thick) and similar items, however, are molded industrially with much shorter cure times (~10–20 sec) at the higher end of the molding temperature range. For transfer molding of UF molding powders, pressures of 4–10 tn/in.² (60–150 MPa), calculated on the area of the transfer pot, are generally recommended.

Special injection grades of UF molding powder have been developed for injection-molding applications which call for molding materials with good flow characteristics between 70°C and 100°C, unaffected by long residence time in the barrel but capable of almost instant cure in the mold cavity at a higher temperature.

Although the transition from compression molding to injection molding has been extensive for phenolics, the same cannot be said for UF Materials, because they are more difficult to mold, possibly because the UF are more brittle than a phenolic resin and so are less able to withstand the stress peaks caused by filler orientation during molding. A combination of compression and injection processes has therefore been developed in which a screw preplasticizing unit delivers preheated and softened material directly to a compression-mold cavity.

4.3.3.2.3 Properties and Applications

The wide color range possible with UF molding powders has been an important reason for the widespread use of the material. These moldings have a number of other desirable features: low cost, good electrical insulation properties, and resistance to continuous heat up to a temperature of 70°C. Some typical values of physical properties of UF molding compositions are given in [Table 4.21](#). They do not impart taste and odor to food-stuffs and beverages with which they come in contact and are resistant to detergents and dry-cleaning solvents.

The foregoing properties account for major uses of UF in two applications, namely, bottle caps and electrical fittings. It is also used for colored toilet seats, vacuum flasks, cups and jugs, hair drier housings,

TABLE 4.21 Properties of Urea-Formaldehyde and Melamine-Formaldehyde Moldings.

Property	Urea-Formaldehyde (α -Cellulose Filled)	Melamine-Formaldehyde (Cellulose Filled)
Specific gravity	1.5–1.6	1.5–1.55
Tensile strength 10 ³ lbf/in. ²	7.5–11.5	8–12
MPa	52–80	55–83
Impact strength (ft.-lbf)	0.20–0.35	0.15–0.24
Dielectric strength (90°C) V/0.001 in.	120–200	160–240
Volume resistivity (ohm-m)	10 ¹³ –10 ¹⁵	10 ⁹ –10 ¹⁰
Water absorption (mg) 24 h at 20°C	50–130	10–50
30 min at 100°C	180–460	40–110

^a Testing according to BS 2782.

Source: Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.

toys, knobs, meat trays, switches, lamp shades, and ceiling light bowls. In the latter applications it is important to ensure adequate ventilation to prevent overheating and consequent cracking of the molded articles.

However, only about 3% of UF resins are used for molding powders. The bulk (about 85%) of the resins are used as adhesives in the particleboard, plywood, and furniture industries. Resins for these applications are commonly available with U/F molar ratios ranging from 1:1.4 to 1:2.2.

To prepare a suitable resin for adhesive applications, urea is dissolved in formalin (initially neutralized to pH 7.5) to give the desired U/F molar ratio. After boiling under reflux for about 15 min to give demethylol urea and other low-molecular products, the resin is acidified, conveniently with formic acid, to pH 4, and reacted for a further period of 5–20 min. The resulting water-soluble resin with approximately 50% solids content is stabilized by neutralizing to a pH 7.5 with alkali. For use as an aqueous solution, as is normally the case, the resin is then partially dehydrated by vacuum distillation to give a 70% solids content.

Phosphoric acid, or more commonly ammonium chloride, is used as a hardener for UF resin adhesives. Ammonium chloride reacts with formaldehyde to produce hexamine and hydrochloric acid, and the latter catalyzes the curing of the resin. In the manufacture of plywood a resin (with U/F molar ratio typically 1:1.8) mixed with hardener is applied to wood veneers, which are then plied together and pressed at 95–110°C under a pressure of 200–800 psi (1.38–5.52 MPa). The UF resin-bonded plywood is suitable for indoor applications but is generally unsuitable for outdoor use. For outdoor applications phenol-formaldehyde, resorcinol-formaldehyde, or melamine-formaldehyde resins are more suitable.

Large quantities of UF resin are used in general wood assembly work. For joining pieces of wood the resin-hardener solution is usually applied to the surfaces to be joined and then clamped under pressure while hardening occurs. Alternatively, the resin may be applied to one surface and the hardener to the other, allowing them to come into contact in situ. This method serves to eliminate pot-life problems of the resin-hardener mixture.

Gap-filling resins are produced by incorporating into UF resins plasticizers, such as furfuryl alcohol, and fillers to minimize shrinkage and consequent cracking and crazing.

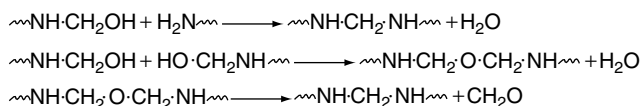
In the manufacture of wood chipboard, which represents one of the largest applications of UF resins, wood chips are mixed with about 10% of a resin-hardener solution and pressed in a multidaylight press at 150°C for about 8 min. Since some formaldehyde is released during the opening of the press, it is necessary to use a resin with a low formaldehyde content. Because it has no grain, a wood chipboard is nearly isotropic in its behavior and so does not warp or crack. However, the water resistance of chipboard is poor.

4.3.3.3 Melamine–Formaldehyde Resins

Monomers	Polymerization	Major Uses
Melamine (trimerization of cyanamide), formaldehyde	Stepwise polycondensation	Dinnerware, table tops, coatings

Reaction of melamine (2,4,6-triamino-1,3,5-triazine) with neutralized formalin at about 80–100°C leads to the production of a mixture of water-soluble methylol melamines. The methylol content of the mixture depends on the initial ratio of formaldehyde to melamine and on the reaction conditions. Methylol melamines possessing up to six methylol groups per molecule are formed (Figure 4.27).

On further heating, the methylol melamines undergo condensation reactions, and a point is reached where hydrophobic resin separates out. The rate of resinification depends on pH. The rate is minimum at about pH 10.0–10.5 and increases considerably both at lower and higher pH. The mechanism of resinification and cross-linking is similar to that observed for urea-formaldehyde (Figure 4.26) and involves methylol–amine and methylol–methylol condensations.



In industrial practice, resinification is carried out to a point close to the hydrophobe point. This liquid resin is either applied to the substrate or dried and converted into molding powder before proceeding with the final cure.

In a typical process [14] a jacketed resin kettle fitted with stirrer and reflux condenser is charged is charged with 240 parts of 40% w/v formalin (pH adjusted to 8.0–8.5 using a sodium carbonate solution) and 126 parts of melamine (to give a melamine–formaldehyde ratio of 1:3), and the temperature is raised to 85°C. The melamine forms methylol derivatives and goes into solution. This water-soluble A-stage resin may be used for treatment of paper, leather, and fabrics to impart crease resistance, stiffness, shrinkage control, water repellency, and fire retardance. It may be spray dried to give a more stable, water-soluble product.

For laminating and other purposes the initial product is subjected to further condensation reactions at about 85°C with continuous stirring for more than 30 min. The hydrophilicity of the resin, as shown by its water tolerance, decreases with increasing condensation. The reaction is usually continued until a stage is reached when addition of 3 cm³ of water will cause 1 cm³ of resin to become turbid. The condensation reactions may be carried out at higher temperatures and lower pH values to achieve this stage more rapidly.

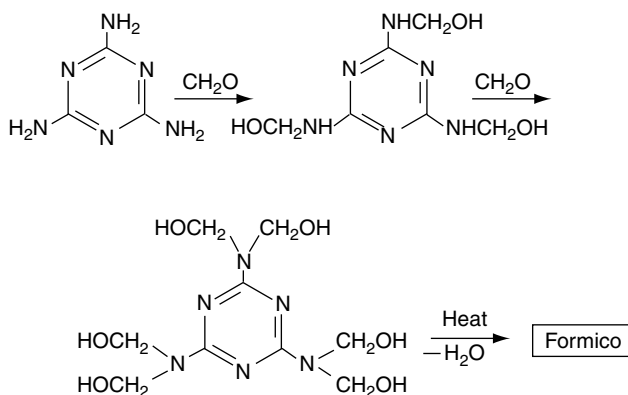


FIGURE 4.27 Reactions in the synthesis of formica.

In aqueous solutions the hydrophobic resins have a shelf life of just a few days. The resin may be diluted with methylated spirit to about 50% solids content and pH adjusted to 9.0–9.5 to achieve greater stability. The addition of about 0.1% borax (calculated on the weight of the solids content) as an aqueous solution is useful in obtaining this pH maintaining it for several months. The stabilized resin is stored preferably at 20–35°C, because too low a storage temperature will cause precipitation and too high at temperature will cause gelation.

Melamine–formaldehyde molding powders are generally prepared by methods similar to those used for UF molding powders. In a typical process an aqueous syrup of MF resin with melamine–formaldehyde ratio of 1:2 is compounded with fillers, pigments, lubricants, stabilizers, and accelerators in a dough-type mixer. The product is then dried and ball-milled by processes similar to those used for UF molding powders.

Alpha-cellulose is used as a filler for the more common decorative molding powders. Industrial-grade MF materials use fillers such as asbestos, silica, and glass fiber. These fillers are incorporated by dry blending methods. The use of glass fiber gives moldings of higher mechanical strength, improved dimensional stability, and higher heat resistance than other fillers. The mineral-filled MF moldings have superior electrical insulation and heat resistance and may be used when phenolics and UF compositions are unsuitable.

MF moldings are superior to UF products in lower water absorption (see [Table 4.21](#)), greater resistance to staining by aqueous solutions such as fruit juices and beverages, better retention of electrical properties in damp conditions, better heat resistance, and greater hardness. Compared with the phenolic resins, MF resins have better color range, track resistance, and scratch resistance. MF resins, are however, more expensive than general-purpose UF and PF resins.

MF compositions are easily molded in conventional compression- and transfer-molding equipment. Molding temperatures from 145°C to 165°C and molding pressures 2–4 tonf/in.² (30–60 MPa) are usually employed. In transfer molding, pressures of 5–10 tonf/in.² (75–150 MPa) are used. The cure time for an 1/8-in.-thick molding is typically 2 1/2 min at 150°C.

Largely because of their wide color range, surface hardness, and stain resistance, MF resins are used as molding compositions for a variety of mechanical parts or household goods and as laminating resins for tops for counters, cabinets, and tables. The mineral-filled molding powders are used in electrical application and knobs and handles for kitchen utensils.

An interesting application of MF resins in compression molding involves decorative foils made by impregnating a printed or decorated grade of paper with resin and then drying. The foil may be applied to a compression molding shortly before the cure is complete, and the resin in the foil may be cured in that position to produce a bonding.

In a typical process of laminating paper layers to make materials useful in electrical applications as well as decorative laminates (best known as *formica*), kraft paper, about the weight used in shopping bags, is run through a solution of melamine–formaldehyde prepolymer. Drying out water or driving off the solvent leave an impregnated sheet that can be handled easily, since the brittle polymer does not leave the surface sticky.

As many as a dozen or more layers are piled up. For decorative purposes a printed rag or decorated cloth paper is put on top and covered with a translucent paper layer. The entire assembly is heated between smooth plates in a high-pressure press to carry out the thermosetting (curing) reaction that binds the sheets together into a strong, solvent-resistant, heat-resistant, and scratch-resistant surfacing material. The laminate, which is only about 1.5-mm thick, can be glued to a plywood base for use in tabletops, countertops, and the like.

4.3.4 Polyurethanes

A *urethane* linkage (–NHCOO–) is formed by the reaction of an isocyanate (–NCO) and an alcohol: $\text{RNCO} + \text{R}'\text{OH} \rightarrow \text{NHCOOR}'$ [14,48,49]. By the same reaction, polyhydroxy materials will react with

polyisocyanates to yield polyurethanes soft thermoplastic elastomers to hard thermoset rigid foams are readily produced from liquid monomers.

The basic building blocks for polyurethanes are polyisocyanates and macroglycols, also called *polyols*. The commonly used polyisocyanates are tolylene-diisocyanate (TDI), diphenylmethane diisocyanate or methylenediphenyl isocyanate (MDI), and polymeric methylenediphenyl isocyanate (PMDI) mixtures manufactured by phosgenating aromatic polyamines derived from the acid-catalyzed condensation of aniline and formaldehyde. MDI and PMDI are produced by the same reaction, and separation of MDI is achieved by distillation. The synthetic routes in the manufacture of commercial polyisocyanates are summarized in Figure 4.28.

A number of specialty aliphatic polyisocyanates have been introduced recently in attempts to produce a light-stable polyurethane coating. Triisocyanate made by reacting hexamethylene diisocyanate with water (Figure 4.28c) is reported to impart good light stability and weather resistance in polyurethane coatings and is probably the most widely used aliphatic polyisocyanate.

The macroglycols used in the manufacture of polyurethanes are either polyether or polyester based. Polyether diols are low-molecular-weight polymers prepared by ring-opening polymerization of olefin oxides (see also the section on polyethers), and commonly used polyester polyols are polyadipates. A polyol produced by ring-opening polymerization of caprolactone, initiated with low-molecular-weight glycols, is also used. The reactions are summarized in Figure 4.29.

Isocyanates are highly reactive materials and enter into a number of reactions with groups or molecules active hydrogen, such as water, amine, and also urethane. Isocyanates are also toxic and care should be exercised in their use. Their main effect is on the respiratory system.

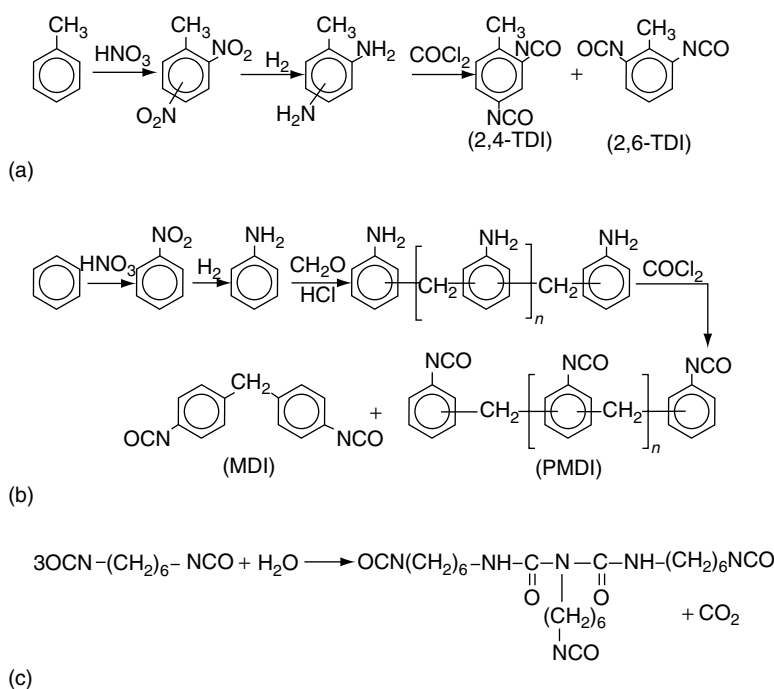


FIGURE 4.28 Reactions used in the manufacture of commercial isocyanates. (a) TDI. (b) PMDI and MDI. (c) Aliphatic triisocyanate.

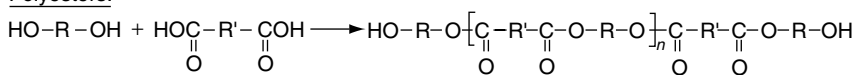
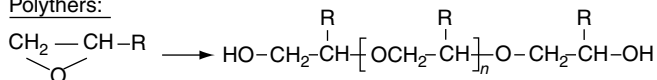
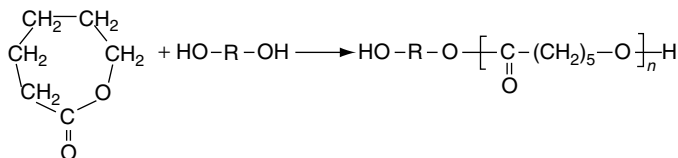
Polyesters:Polyethers:Polycaprolactone

FIGURE 4.29 Reactions used in the manufacture of macroglycols.

Major polyurethane products today include cellular materials such as water-blown flexible foams or fluorocarbon-blown rigid foams, elastomers, coatings, and elastic fibers, which are described subsequently. Closely related to polyurethanes is an isocyanate-based product called *isocyanurate foam*.

4.3.4.1 Polyurethane Rubbers and Spandex Fibers

By careful formulations it is possible to produce polyurethane rubbers with a number of desirable properties [50]. The rubbers can be thermoplastic (linear) or thermoset (slightly cross-linked) products.

4.3.4.1.1 Cross-Linked Polyurethane Rubbers

The starting point in the preparation of this type of rubber, typified by Vulkollan rubbers, is a polyester prepared by reacting a glycol such as ethylene or propylene glycol with adipic acid. The glycol is in excess so that the polyester formed has hydroxyl end groups. This polyester macroglycol is then reacted with an excess of a diisocyanate such as 1,5-naphthalene diisocyanate or MDI (Figure 4.28). The molar excess of diisocyanate is about 30%, so the number of polyesters joined together is only about 2–3, and the resulting prepolymer has isocyanate end groups (see Figure 4.30a).

The prepolymer can be chain extended with water, glycols, or amines which link up prepolymer chains by reacting with terminal isocyanate groups (see Figure 4.30b). (The water reaction liberates carbon dioxide, so it must be avoided in the production of elastomers, but it is important in the manufacture of foams.) The urea and urethane linkages formed in the chain extension reactions also provide sites for branching and cross-linking, since these groups can react with free isocyanate or terminal isocyanate groups to form *biuret* and *allophanate* linkages, respectively (see Figure 4.30c). Biuret links, however, predominate since the urea group reacts faster than the urethane groups. The degree of cross-linking can to some extent be controlled by adjusting the amount of excess isocyanate, whereas more highly cross-linked structures may be produced by the use of a triol in the initial polyester.

Vulkollan-type rubbers suffer from the disadvantage that the prepolymers are unstable and must be used within a day or two of their production. Moreover, these rubbers cannot be processed with conventional rubber machineries, so the products are usually made by a casting process. Attempts were then made to develop other polyurethane rubbers which could be processed by conventional techniques.

One approach was to react the diisocyanate with a slight excess of polyester so that the prepolymer produced has terminal hydroxyl groups. The prepolymers are rubberlike gums and can be compounded

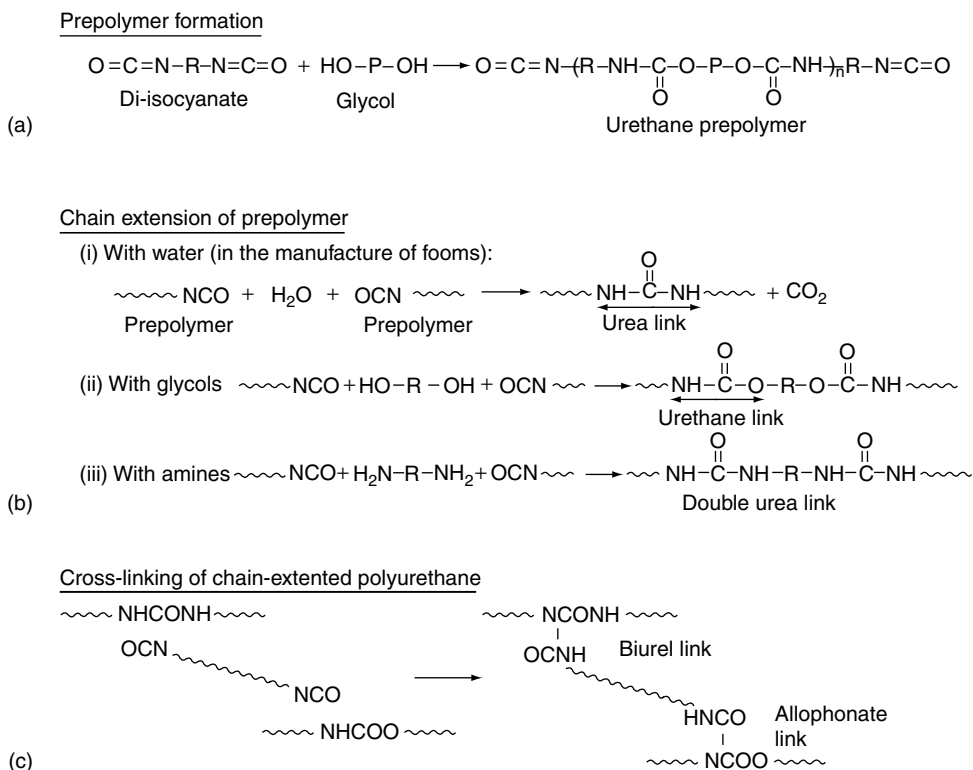


FIGURE 4.30 Equations for preparation, chain extension, and curing of polyurethanes.

with other ingredients on two-roll mills. Final curing can be done by the addition of a diisocyanate or, preferably, a latent diisocyanate, i.e., a substance which produces an active diisocyanate under the conditions of molding. Polyurethane rubbers of this class are exemplified by Chemigum SL (Goodyear), Desmophen A (Bayer), and Daltoflex 1 (ICI), which used polyester–amide for the manufacture of prepolymer.

Another approach was adopted by Du Pont with the product Adiprene C, a polyurethane rubber with unsaturated groups that allow vulcanization with sulfur.

Polyurethane rubbers, in general, and the Vulkollan-type rubbers, in particular, possess certain outstanding properties. They usually have higher tensile strengths than other rubbers and possess excellent tear and abrasion resistance. The urethane rubbers show excellent resistance to ozone and oxygen (in contrast to diene rubbers) and to aliphatic hydrocarbons. However, they swell in aromatic hydrocarbons and undergo hydrolytic decomposition with acids, alkalis, and prolonged action of water and steam.

Though urethane rubbers are more costly than most of other rubbers, they are utilized in applications requiring superior toughness and resistance to tear, abrasion, ozone, fungus, aliphatic hydrocarbons, and dilute acids and bases. In addition, they excel in low-temperature impact and flexibility. Urethane rubbers have found increasing use for forklift tires, shoes soles and heels, oil seals, diaphragms, chute linings, and a variety of mechanical applications in which high elasticity is not an important prerequisite.

Emphasis on reaction injection-molding (RIM) technology in the automotive industry to produce automotive exterior parts has created a large potential for thermoset polyurethane elastomers. *Reaction injection molding*, originally known as reaction casting, is a rapid, one-step process to produce thermoset polyurethane products from liquid monomers. In this process liquid monomers are mixed under high pressure prior to injection into the mold. The polymerization occurs in the mold. Commercial RIM

polyurethane products are produced from MDI, macroglycols, and glycol or diamine extenders. The products have the rigidity of plastics and the resiliency of rubber.

Later advances include short, glass-fiber reinforced, high-modulus (flexural modulus greater than 300,000 psi, i.e., 2070 MPa) polyurethane elastomers produced by the reinforced RIM process. These reinforced high-modulus polyurethane elastomers are considered for automotive door panels, trunk lids, and fender applications.

Though originally developed for the automotive industry for the production of car bumpers, the RIM process has found its greatest success in the shoe industry, where semiflexible polyurethane foams have proved to be good soling materials.

4.3.4.1.2 Thermoplastic Polyurethane Rubbers

The reactions of polyols, diisocyanates, and glycols, as described, do tend to produce block copolymers in which hard blocks with glass transition temperatures well above normal ambient temperature are separated by soft rubbery blocks. These polymers thus resemble the SBS triblock elastomers and, more closely, the polyether-ester thermoplastic elastomers of the Hytrel-type described earlier.

In a typical process of manufacturing thermoplastic polyurethane elastomers, a prepolymer is first produced by reacting a polyol, such as linear polyester with terminal hydroxyl groups, or a hydroxyl-terminated polyether, of molecular weights in the range of 800–2500, with an excess of diisocyanate (usually of the MDI type) to give a mixture of isocyanate-terminated polyol prepolymer and free (unreacted) diisocyanate. This mixture is then reacted with a chain extender such as 1,4-butanediol to give a polymer with long polyurethane segments whose block length depends on the extent of excess isocyanate and the corresponding stoichiometric glycol.

The overall reaction is shown in Figure 4.31a. Provided that R (in free diisocyanate) and R' (in glycol) are small and regular, the polyurethane segments will show high intersegment attraction (such as hydrogen bonding) and may be able to crystallize, thereby forming hard segments. In such polymers hard segments with T_g well above normal ambient temperature are separated by polyol soft segments, which in the mass are rubbery in nature. Hard and soft segments alternate along the polymer chain. This structure closely resembles that of polyester-polyether elastomers (Figure 4.11). Similar reactions occur when an amine is used instead of a glycol as a chain extender (see Figure 4.31b). The polymer in this case has polyurea hard segments separated by polyol soft segments.

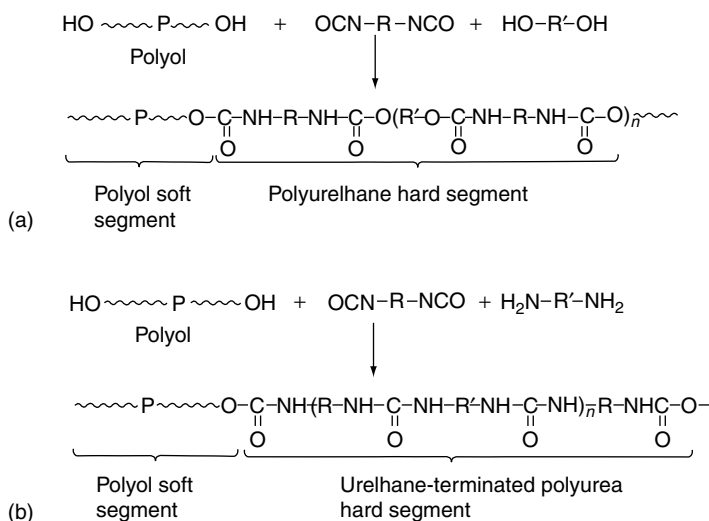


FIGURE 4.31 Reactions for the manufacture of polyurethane block copolymers.

The polymers produced by these reactions are mainly thermoplastic in nature. Though it is possible that an excess of isothiocyanate may react with urethane groups in the chain to produce allophanate cross-links (see Figure 4.30c), these cross-links do not destroy the thermoplastic nature of the polymer because of their thermal lability, i.e., breaking down on heating and reforming on cooling. However, where amines have been used as chain extenders, urea groups are produced (Figure 4.31b), which, on reaction with excess isocyanate, may give the more stable biuret cross-links (see Figure 4.30c).

Many of the commercial materials designated as thermoplastic polyurethanes are in reality slightly cross-linked. This cross-linking may be increased permanently by a post-curing reaction after shaping. The polyurethane product Estane (Goodrich) may, however, be regarded as truly thermoplastic. The thermoplastic rubbers have properties similar to those of Vulkollan-type cast polyurethane rubbers, but they have higher values for compression set.

Thermoplastic polyurethane elastomers can be molded and extruded to produce flexible articles. Applications include wire insulation, hose, tracks for all-terrain vehicles, solid tires, roller skate wheels, seals, bushing, convoluted bellows, bearings, and small gears for high-load applications. In the automobile industry thermoplastic polyurethanes are used primarily for exterior parts. Their ability to be painted with flexible polyurethane-based paints without pretreatment is valuable.

4.3.4.1.3 Spandex Fibers

One particular form of thermoplastic polyurethane elastomers is the elastic fiber known as Spandex. The first commercial material of this type was introduced by Du Pont in 1958 (Lycra). It is a relatively high-priced elastomeric fiber made on the principle of segmented copolymers. Here again the soft block is a polyol, and the hard block is formed from MDI (4,4'-diisocyanatodiphenyl methane) and hydrazine. The reactions are shown in Figure 4.32. Note that this fiber-forming polymer contains urethane and semicarbazide linkages in the chain. The product is soluble in amide solvent, and the fiber is produced by dry spinning from a solution. Major end uses of Lycra are in apparel (swimsuits and foundation garments).

Subsequently several other similar materials have been introduced, including Dorlastan (Bayer), Spanzelle (Courtaulds), and Vyrene (U.S. Rubber).

The polyol component with terminal hydroxyl groups used in the production of the foregoing materials may be either a polyether glycol or a polyester glycol (see Figure 4.29). For example, Du Pont uses polytetrahydrofuran (a polyether glycol) for Lycra. U.S. Rubber originally used a polyester of molecular weight of about 2000, obtained by condensation of adipic acid with a mixture of ethylene

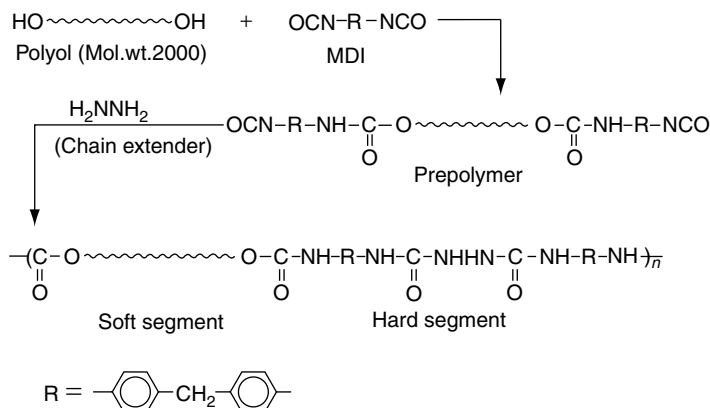


FIGURE 4.32 Reactions for the manufacture of segmented elastomeric fiber (Lycra).

glycol and propylene glycol, and a polyether-based mixture was used for Vyrene 2, introduced in 1967. These polyols are reacted with an excess of diisocyanate to yield an isocyanate-terminated prepolymer which is then chain extended by an amine such as hydrazine (NH_2NH_2) or ethylenediamine (see [Figure 4.32](#)). Fibers are usually spun from solution in dimethylformamide.

Possessing higher modulus, tensile strength, resistance to oxidation, and ability to be produced at finer deniers, spandex fibers have made severe inroads into the natural rubber latex thread market. Major end uses are in apparel. Staple fiber blends with nonelastic fibers have also been introduced.

4.3.4.2 Flexible Polyurethane Foam

Although polyurethane rubbers are specialty products, polyurethane foams are well known and widely used materials [51]. About half of the weight of plastics in modern cars is accounted for by such forms.

Flexible urethane foam is made in low densities of 1–1.2 lb/ft³ (0.016–0.019 g/cm³), intermediate densities of 1.2–3 lb/ft³ (0.019–0.048 g/cm³), high resilience (HR) foams of 1.8–3 lb/ft³ (0.029–0.048 g/cm³), and semiflexible foams of 6–12 lb/ft³ (0.096–0.192 g/cm³). Filled foams of densities as high as 45 lb/ft³ (0.72 g/cm³) have also been made.

In many respects the chemistry of flexible urethane foam manufacture is similar to that of the Vulkollan-type rubbers except that gas evolution reactions are allowed to occur concurrently with chain extension and cross linking (see [Figure 4.30](#)). Most flexible foams are made from 80/20 TDI, which refers to the ratio of the isomeric 2,4-tolylendiisocyanate to 2,6-tolylendiisocyanate. Isocyanates for HR foams are about 80% 80/20 TDI and 20% PMDI, and those for semiflexible foams are usually 100% PMDI.

Polyols usually are polyether based, since these are cheaper, give greater ease of foam processing, and provide more hydrolysis resistance than polyesters. Polyether polyols can be diols, such as polypropylene glycols with molecular weight of about 2000, or triols with molecular weight of 3000–6000. The most common type of the latter is triol adduct of ethylene oxide and propylene oxide with glycerol with a molecular weight of 3000. For HR foams polyether triols with molecular weight of 4500–6000 made by reacting ethylene oxide with polypropylene oxide based triols, are used.

The reaction of isocyanate and water that evolves carbon dioxide (see [Figure 4.30b](#)) is utilized for foaming in the production of flexible foams. The density of the product, which depends on the amount of gas evolved, can be reduced by increasing the isocyanate content of the reaction mixture and by correspondingly increasing the amount of water to react with the excess isocyanate. For greater softness and lower density some fluorocarbons (F-11) may be added in addition to water.

The processes for producing flexible polyurethane foams have been described in [Chapter 2](#).

4.3.4.2.1 Applications

The largest-volume use of flexible foam is furniture and bedding, which account for nearly 47% of the flexible polyurethane foam market. Almost all furniture cushioning is polyurethane. Automobile seating is either made from flexible slabstock or poured directly into frames, so-called deep seating, using HR chemical formulations. Semiflexible polyurethane foams find use in crash pads, arm and head rests, and door panels.

Much flexible foam is used in carpet underlay. About 43% is virgin foam, and 57% is scrap rebounded with adhesives under heat and pressure.

Thermal interlining can be made by flame bonding thin-sliced, low-density (1–1.5 lb/ft³) polyester-based fabric. The flame melts about one-third of the foam thickness, and the molten surface adheres to the fabric.

Flexible foams also find use in packaging applications. Die-cut flexible foam is used to package costly goods such as delicate instruments, optical products, and pharmaceuticals. Semiflexible foam lining is used for cart interiors to protect auto and machine parts during transportation.

4.3.4.3 Rigid and Semirigid Polyurethane Foams

Most rigid foam is made from polymeric isocyanate (PMDI) and difunctional polyether polyols. PMDI of functionality 2.7 (average number of isocyanate groups per molecules) is used in insulation foam manufacturing. Functionalities greater than two contribute rigidity through cross-linking. Higher-functionality, low-molecular-weight polyols are sometimes added because they contribute rigidity by cross-linking and short chain length. Such polyols are made by reaction of propylene oxide with sucrose, pentaerythritol, or sorbitol.

Rigid insulation foams are usually hydrocarbon blown to produce a closed-cell foam with excellent insulation properties. High-density foams are water blown where structural and screw-holding strength is needed, and halocarbons are used as blowing agents when high-quality, decorative surfaces are required. A compromise between these two aims can be achieved by the addition of water to halocarbon-blown formulations.

Formulation, processing methods, properties, and applications of rigid and semirigid polyurethane foams have been described in have been described in [Chapter 2](#). Major use of these foams are in building and construction (56%), transportation (12%), furniture, and packaging. Low-density, rigid foam is the most efficient thermal insulation commercially available and is extensively used in building construction. In transportation, urethane insulation is used in rail cars, containers, truck trailer bodies, and in ships for transporting liquefied natural gas. This requires thinner insulation and so yields more cargo space. Rigid foam is also used to give flotation in barge compartments.

High-density rigid foam, 5–15 lb/ft³ (0.08–0.24 g/cm³), is used for furniture items such as TV and stereo cabinets, chair shells, frames, arms, and legs, cabinet drawer fronts and doors, and mirror and picture frames. RIM-molded, integral-skin, high-density foams with core densities of 10–20 lb/ft³ (0.16–0.32 g/cm³) and skin densities of 55–65 lb/ft³ (0.88–1.04 g/cm³) are used in electronic, instrument, and computer cabinets.

Industrial uses of rigid foams include commercial refrigeration facilities as well as tanks and pipelines for cryogenic transport and storage.

4.3.4.3.1 Polyisocyanurates

Though closed-cell rigid polyurethane foams are excellent thermal insulators, they suffer from the drawback of unsatisfactory fire resistance even in the presence of phosphorus- and halogen-based fire retardants. In this context, polyisocyanurates, which are also based on isocyanates, have shown considerable promise. Isocyanurate has greater flame resistance than urethane. Although rigid polyurethane is specified for the temperatures up to 200°F (93°C), rigid polyisocyanurate foams, often called *trimer foams*, withstand use temperatures to 300°F (149°C). Physical properties and insulation efficiency are similar for both types.

The underlying reaction for polyisocyanurate formation is trimerization of an isocyanate under the influence of specific catalysts ([Figure 4.33a](#)). The most commonly used is a polymeric isocyanate (PMDI) prepared by reacting phosgene with formaldehyde–aniline condensates, as shown in [Figure 4.28b](#).

PMDIs are less reactive than monomeric diisocyanate but are also less volatile. The polyisocyanurate produced from this material will be of type shown in [Figure 4.33b](#). Some of the catalysts used for the polytrimerization reactions are alkali-metal phenolates, alcoholates and carboxylates, and compounds containing *o*-(dimethylaminomethyl)-phenol groups.

To produce foams, fluorocarbons such as trichlorofluoromethanes are used as the sole blowing agents. Polyisocyanurate foams may be prepared by using standard polyurethane foaming equipment and a two-component system, with isocyanate and fluorocarbon forming one component and the activator or activator mixture forming the second component.

Because of the high cross-link density of polyisocyanurates, the resultant foam tends to be brittle. Consequently, there has been a move toward making polyisocyanurate–polyurethane combinations. For example, the isocyanate trimerization reaction has been carried out with isocyanate end-capped TDI-based prepolymers to make isocyanurate-containing polyurethane foams. Isocyanate trimerization in the

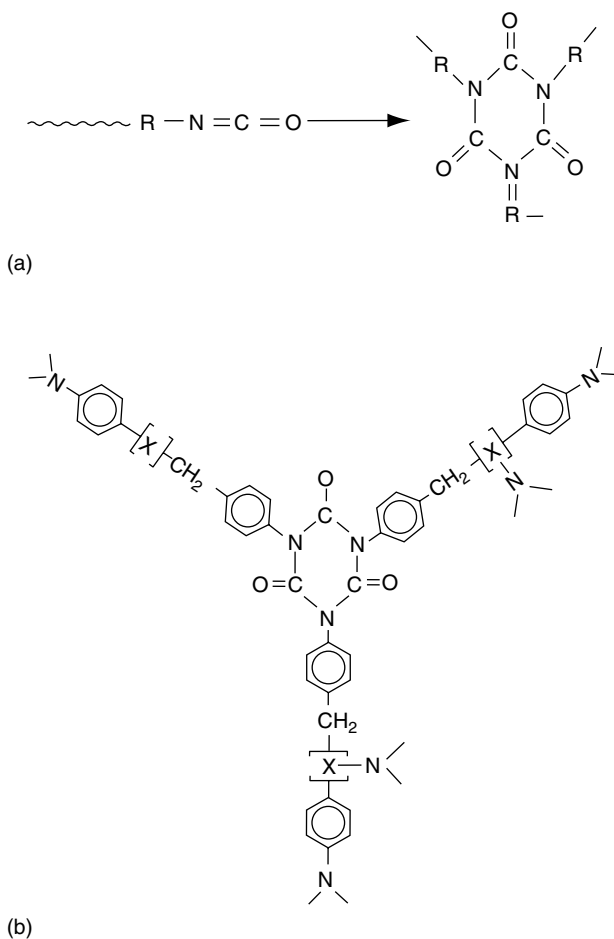


FIGURE 4.33 (a) Trimerization of an isocyanate. (b) Structure of polyisocyanurate produced from polymeric MDIs.

presence of polyols of molecular weights less than 300 has also been employed to produce foams by both one-shot and prepolymer methods.

4.3.4.4 Polyurethane Coatings

Polyurethane systems are also formulated for surface-coating applications. A wide range of such products has become available. These include simple solutions of finished polymer (linear polyurethanes), One component systems containing blocked isocyanates, two-component systems based on polyester and isocyanate or polyether and isocyanate, and a variety of prepolymer and adduct systems.

Coatings based reapon TDI and MDI gradually discolor upon exposure to light and oxygen. In contrast, aliphatic diisocyanates such as methylene dicyclohexyl isocyanate, hexamethylene diisocyanate derivatives, and isophorone diisocyanate all produce yellowing resistant, clear, or color-stable pigmented coatings. Of the polyols used, half are polyester type and half are polyether types. The coatings can vary considerably in hardness and flexibility, depending on formulation.

Polyurethane coatings are used wherever applications require toughness, abrasion resistance, skin flexibility, fast curing, good adhesion, and chemical resistance. Use include metal finishes in chemical plants, wood finishes for boats and sports equipment. finishes for rubber goods. and rainerosion resistant coatings for aircraft.

TABLE 4.22 Blocked Isocyanates for One-Component System

Blocking Agent	Unblocking Temperature	
	°C	°F
Phenol	160	320
<i>m</i> -Nitrophenol	130	266
Acetone oxime	180	356
Diethyl malonate	130–140	266–284
Caprolactam	160	320
Hydrogen cyanide	120–130	248–266

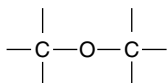
The one-component coating systems require blocking of the isocyanate groups to prevent polymerization in the container. Typical blocking agents are listed in Table 4.22.

Generation of the blocking agent upon heating to cause polymerization is a disadvantage of blocked one-component systems. This problem can be overcome by using a masked aliphatic diisocyanate system, as shown in Figure 4.34. The cyclic bisurea derivative used in such a system is stable in the polyol or in water emulsion formulated with the polyol at ordinary temperatures. Upon heating, ring opening occurs, generating the diisocyanate, which reacts instantaneously with the macroglycol in form a polyurethane coating.

Polyurethane adhesives involving both polyols and isocyanates are used. These materials have found major uses in the boot and shoe industry.

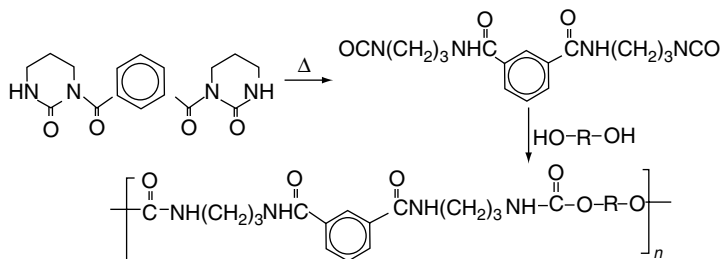
4.3.5 Ether Polymers

For the purposes of this chapter ether polymers or polyethers are defined as polymers which contain recurring ether groupings in their backbone structure:



Polyethers are obtained from three different classes of monomers, namely, carbonyl compounds, cyclic ethers, and phenols. They are manufactured by a variety of polymerization processes, such as polymerization (polyacetal), ring-opening polymerization (polyethylene oxide, polypropylene oxide, and epoxy resins), oxidative coupling (Polyphenylene oxide), and polycondensation (polysulfone).

Polyacetal polyphenylene oxide are widely used as engineering thermoplastics, and epoxy resins are used in adhesive and casting application. The main uses of poly(ethylene oxide) and poly(propylene oxide) are as macroglycols in the production of polyurethanes. Polysulfone is one of the high-temperature-resistant engineering plastics.

**FIGURE 4.34** Reactions of macrocyclic ureas used as masked diisocyanates.

4.3.5.1 Polyacetal



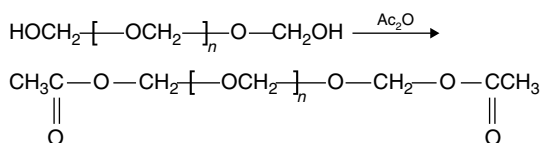
Monomers	Polymerization	Major Uses
Formaldehyde, trioxane	Cationic or anionic chain polymerization	Appliances, plumbing and hardware, transportation

Polyoxymethylene (polyacetal) is the polymer of formaldehyde and is obtained by polymerization of aqueous formaldehyde or ring-opening polymerization of trioxane (cyclic trimer of formaldehyde, melting point 60–60°C), the latter being the preferred method [52]. This polymerization of trioxane is conducted in bulk with cationic initiators. In contrast, highly purified formaldehyde is polymerized in solution using either cationic or anionic initiators.

Polyacetal strongly resembles polyethylene in structure, both polymers being linear with a flexible chain backbone. Since the structures of both the polymers are regular and the question of tacticity does not arise, both polymers are capable of high degree of crystallization. However, the acetal polymer molecules have a shorter backbone (—C—O—) bond and so pack more closely together than polyethylene molecules. The acetal polymer is thus harder and has a higher melting point (175°C for the homopolymer).

Being crystalline and incapable of specific interaction with liquids, acetal homopolymer resins have outstanding resistance to organic solvents. No effective solvent has yet been found for temperatures below 70°C (126°F). Above this temperature, solution occurs in a few solvents such as chlorophenols. Swelling occurs with solvents of similar solubility parameter to that of the polymer [$\delta = 11.1 \text{ (cal/cm}^3)^{1/2} = 22.6 \text{ MPa}^{1/2}$]. The resistance of polyacetal to inorganic reagents is not outstanding, however. Strong acids, strong alkalis, and oxidizing agents cause a deterioration in mechanical properties.

The ceiling temperature for the acetal polymer is 127°C. Above this temperature the thermodynamics indicate that depolymerization will take place. Thus it is absolutely vital to stabilize the polyacetal resin sufficiently for melt processing at temperature above 200°C. Stabilization is accomplished by capping the thermolabile hydroxyl end groups of the macromolecule by etherification or esterification, or by copolymerizing with small concentrations of ethylene oxide. These expedients retard the initiation or propagation steps of chain reaction that could cause the polymer to unzip to monomer (formaldehyde). End-group capping is more conveniently achieved by esterification using acetic anhydride.



If formaldehyde is copolymerized with a second monomer, which is a cyclic ether such as ethylene oxide and 1,3-dioxolane, end-group capping is not necessary. The copolymerization results in occasional incorporation of molecules containing two successive methylene groups, whereby the tendency of the molecules to unzip is markedly reduced. This principle is made use of in the commercial products marketed as Celcon (Celanese), Hostaform (Farbwerke Hoechst), and Duracon (Polyplastic).

Degradation of polyacetals may also occur by oxidative attack at random along the chain leading to chain scission and subsequent depolymerization (unzipping). Oxidative chain scission is reduced by the use of antioxidants (see [Chapter 1](#)), hindered phenols being preferred. For example, 2,2'-methylene-bis(4-methyl-6-*t*-butylphenol) is used in Celcon (Celanese) and 4,4'-butylidene bis(3-methyl-6-*t*-butylphenol) in Delrin (Du Pont).

Acid-catalyzed cleavage of the acetal linkage can also cause initial chain scission. To reduce this acid acceptors are believed to be used in commercial practice. Epoxides, nitrogen-containing compounds, and basic salts are all quoted in the patent literature.

Polyacetal is obtained as a linear polymer (about 80% crystalline) with an average molecular weight of 30,000–50,000. Comparative values for some properties of typical commercial products are given in Table 4.23. The principal features of acetal polymers which render them useful as engineering thermoplastics are high stiffness, mechanical strength over a wide temperature range, high fatigue endurance, resistance to creep, and good appearance. Although similar to nylons in many respects, acetal polymers are superior to them in fatigue resistance, creep resistance, stiffness, and water resistance (24-h water absorption at saturation being 0.22% for acetal copolymer vs. 8.9% for nylon-6,6). The nylons (except under dry conditions) are superior to acetal polymers in impact toughness. Various tests indicate that the acetal polymers are superior to most other plastics and die cast aluminum.

The electrical properties of the acetal polymers may be described as good but not outstanding. They would thus be considered in applications where impact toughness and rigidity are required in addition to good electrical insulation characteristics.

The end-group capped acetal homopolymer and the trioxane-based copolymers are generally similar in properties. The copolymer has greater thermal stability, easier moldability, better hydrolytic stability at elevated temperatures, and much better alkali resistance than the homopolymer. The homopolymer, on the other hand, has slightly better mechanical properties, e.g., higher flexural modulus, higher tensile strength, and greater surface hardness.

Acetal polymers and copolymers are engineering materials and are competitive with a number of plastics materials, nylon in particular, and with metals. Acetal resins are being used to replace metals because of such desirable properties as low weight (sp. gr. 1.41–1.42), corrosion resistance, resistance to fatigue, low coefficient of friction, and ease of fabrication.

The resins may be processed without difficulty on conventional injection-molding, blow-molding, and extrusion equipment. The acetal resins are used widely in the molding of telephone components, radios, small appliances, links in conveyor belts, molded sprockets and chains, pump housings, pump impellers, carburetor bodies, blower wheels, cams, fan blades, check valves, and plumbing components such as valve stems and shower heads.

TABLE 4.23 Typical Values for Some Properties of Acetal Homopolymers and Copolymers

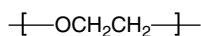
Property	Acetal Homopolymer	Acetal Copolymer
Specific gravity	1.425	1.410
Crystalline melting point (°C)	175	163
Tensile strength (23°C)		
lbf/in. ²	10,000	8500
MPa	70	58
Flexural modulus (23°C)		
lbf/in. ²	410,000	360,000
MPa	2800	2500
Deflection temperature (°C)		
at 264 lbf/in. ²	100	110
at 66 lbf/in. ²	170	158
Elongation at break (23°C) (%)	15–75	23–35
Impact strength (23°C)		
ft.-lbf/in. notch	1.4–2.3	1.1
Hardness, Rockwell M	94	80
Coefficient of friction	0.1–0.3	0.2
Water absorption (%)		
24-h immersion	0.4	0.22
50% RH equilibrium	0.2	0.16
Continuous immersion equilibrium	0.9	0.8

Source: From Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.

Because of their light weight, low coefficient of friction, absence of slipstick behavior, and ability to be molded into intricate shapes in one piece, acetal resins find use as bearings. The lowest coefficient of friction and wear of acetal resin are obtained against steel.

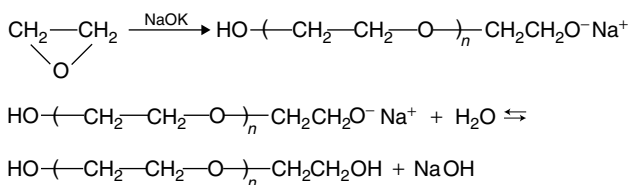
Through counted as one of the engineering plastics, acetal resins with their comparatively high cost cannot, however, be considered as general-purpose thermoplastics in line with polyethylene, polypropylene, PVC, and polystyrene

4.3.5.2 Poly(Ethylene Oxide)



Monomer	Polymerization	Major Uses
Ethylene oxide	Ring-opening polymerization	<p>Molecular weights 200 – 600—surfactants, humectants, lubricants</p> <p>Molecular weights > 600—pharmaceutical and cosmetic bases, lubricants, mold release agents</p> <p>Molecular weights 10^5 to 5×10^6—water-soluble packaging films and capsules</p>

Poly(ethylene oxide) of low molecular weight, i.e., below about 3000, are generally prepared by passing ethylene oxide into ethylene glycol at 120–150°C (248–302 F) and about 3 atm pressure (304 kPa) by using an alkaline catalyst such as sodium hydroxide [53]. Polymerization takes place by an anionic mechanism.



The polymers produced by these methods are thus terminated mainly by hydroxyl groups and are often referred to as *polyethylene glycols* (PEGs). Depending on the chain length, PEGs range in physical form at room temperature from water white viscous liquids (mol. wt. 200–700), through waxy semisolids (mol. wt. 1000–2000), to hard, waxlike solids (mol. wt. 3000–20,000 and above). All are completely soluble in water, bland, nonirritating, and very low in toxicity; they possess good stability, good lubricity, and wide compatibility.

Since PEGs form a homologous series of polymers, many of their properties vary in a continuous manner with molecular weight. The freezing temperature, which is less than -10°C for PEG of molecular weight 300, rises first rapidly with molecular weight through the low-molecular-weight grades, then increases more gradually through the solids while approaching 66°C , the true crystalline melting point for very high-molecular-weight poly(ethylene oxide) resins.

Other examples of such continuous variations are the increase in viscosity, flash points, and fire points with an increase in molecular weight and a slower increase in specific gravity. In a reverse relationship, hygroscopicity decreases as molecular weight increases, as does solubility in water.

In 1958, commercial poly(ethylene oxide)s of very high molecular weight became available from Union Carbide (trademark Polyox). Two Japanese companies, Meisei Chemical Works, Ltd., and Seitetsu Kagaku Company, Ltd., have begun producing poly(ethylene oxide) under the trademarks Alkox and PEO, respectively. Heterogeneous catalyst systems, which are mainly of two types, namely, alkaline earth

compounds (e.g., oxides and carbonates of calcium, barium, and strontium) and organometallic compounds (e.g., aluminum and zinc alkyls and alkoxides, usually with cocatalysts) are used in their manufacture.

Commercial poly(ethylene oxide) resins supplied in the molecular weight range 1×10^5 – 5×10^6 are dry, free-flowing, white powders soluble in an unusually broad range of solvents. The resins are soluble in water at temperatures up to 98°C and also in a number of organic solvents, which include chlorinated hydrocarbons such as carbon tetrachloride and methylene chloride, aromatic hydrocarbons such as benzene and toluene, ketones such as acetone and methyl ethyl ketone, and alcohols such as methanol and isopropanol.

4.3.5.3 Applications

4.3.5.3.1 Polyethylene Glycol

The unusual combination of properties of PEGs has enabled them to find a very wide range of commercial uses as cosmetic creams, lotions, and dressings; textile sizes; paper-coating lubricants; pharmaceutical sales, ointments, and suppositories, softeners and modifiers; metal-working lubricants; detergent modifiers; and wood impregnates. In addition, the chemical derivatives of PEGs, such as the mono- and diesters of fatty acids, are widely used as emulsifiers and lubricants.

The PEGs themselves show little surface activity, but when converted to mono- and diesters by reaction with fatty acids, they form a series of widely useful nonionic surfactants. The required balance of hydrophilic–hydrophobic character can be achieved by suitable combination of the molecular weight of the PEG and the nature of the fatty acid. For large-volume items a second production route of direct addition of ethylene oxide to the fatty acids is often preferred. End uses for the fatty esters are largely as textile lubricants and softeners and as emulsifiers in food products, cosmetics, and pharmaceuticals.

The PEGs have found a variety of uses in pharmaceutical products. Their water solubility, blandness, good solvent action for many medicaments, pleasant and nongreasy feel on the skin, and tolerance of body fluids are the reasons why they are frequently the products of choice. Blends of liquid and solid grades are often selected because of their desirable petrolatum like consistency.

An especially important example of pharmaceutical application of PEGs is as bases for suppositories, where the various molecular grades can be blended to provide any desired melting point, degree of stability, and rate of release of medication. The fatty acid esters of the PEGs are often used in pharmaceuticals as emulsifiers and suspending agents because of their nonionic, blandness, and desirable surface activity. The solid PEGs also find use as lubricants and binders in the manufacture of medicinal tablets.

The PEGs, providing they contain not over 0.2% ethylene and diethylene glycols, are permitted as food additives. The PEG fatty acid esters are especially useful emulsifying agents in food products.

For many of the same reasons which account for their use in pharmaceuticals, the PEGs and their fatty acid esters find many applications in cosmetics and toiletries. Their moisturizing, softening, and skin-smoothing characteristics are especially useful. Typical examples of applications are shaving creams, vanishing creams, toothpastes, powders, shampoos, hair rinses, suntan lotions, pomades and dressings, deodorants, stick perfumes, rouge, mascara, and so on. The nonionic surface-active PEG fatty acid esters find use in a variety of detergents and cleaning compositions.

Liquid PEGs, solid PEGs, or their solutions are often used in a variety of ink preparations, such as thixotropic inks for ballpoint pens, water-based stencil inks, steam-set printing inks, and stamp-pad inks.

There are numerous other industrial uses for the PEGs in which they serve primarily as processing aids and do not remain as integral components of the products. The PEGs add green strength and good formability to various ceramic components of the products. The PEGs add green strength and good formability to various ceramic compositions to be stamped, extruded, or molded. They can be burned out cleanly during subsequent firing operations.

In electroplating baths small amounts of PEGs improve smoothness and grain uniformity of the deposited coatings. Solid PEGs are effective lubricants in paper-coating compositions and promote better

gloss and smoothness in calendaring operations. PEGs, and more particularly their fatty acid esters, are quite widely used as emulsifiers, lubricants, and softeners in textile processing.

PEGs and their esters find use as components of metal corrosion inhibitors in oil wells where corrosive brines are present. Fatty acid esters of PEGs are useful demulsifiers for crude oil–water separation.

The water solubility, nonvolatility, blandness, and good lubricating abilities are some of the reasons for the use of PEGs in metal-working operations. Metal-working lubricants for all but the most severe forming operations are made with the PEGs or with their esters or other derivatives.

4.3.5.3.2 Poly(Ethylene Oxide)

Since their commercialization in 1958, the reported and established applications for high-molecular-weight poly(ethylene oxide) resins have been numerous and diversified. Table 4.24 summarizes in alphabetical order the main applications of these resins in various industries.

In addition to their water solubility and blandness, the main functions and effects of poly(ethylene oxide) resins which lead to these diverse applications are lubrication, flocculation, thickening, adhesion, hydrodynamic drag reduction, and formation of association complexes.

The resins are relatively nontoxic and have a very low level of biodegradability (low BOD). Poly(ethylene oxide) resins with molecular weights from 1×10^5 to 1×10^7 have a very low level of oral toxicity and are not readily absorbed from the gastrointestinal tract. The resins are relatively nonirritating to the skin and have a low sensitizing potential.

Poly(ethylene oxide) resins can be formed into various shapes by using conventional thermoplastic processing techniques. Commercially, thermoplastic processing of these resins has been, however, limited almost exclusively to the manufacture of film and sheeting. Generally, the medium-molecular-weight resins (4×10^5 – 6×10^5) possess melt rheology best suited to thermoplastic processing. The films are produced by calendaring or blown-film extrusion techniques. Usually produced in thicknesses from 1 to 3 mils, the films have very good mechanical properties combined with complete water solubility.

TABLE 4.24 Applications of Poly(Ethylene Oxide) Resins

Industry	Applications
Agriculture	Water-soluble seed tapes Water-soluble packages for agricultural chemicals Hydrogels as soil amendments to increase water retention Soil stabilization using association complexes with poly(acrylic acid) Drift control agent for sprays
Ceramics and glass	Binders for ceramics Size for staple glass-fiber yarns
Chemical	Dispersant and stabilizer in aqueous suspension polymerization
Electrical	Water-soluble, fugitive binder for microporous battery and fuel-cell electrodes
Metals and mining	Flocculant for removal of silicas and clays in hydrometallurgical processes Flocculant for clarification of effluent streams from coal-washing plants
Paper	Filler retention and drainage aid in the manufacture of paper Flocculant for clarification of effluent water
Personal-care products	Lubricant and toothpaste Tickener in preparation of shaving stick Ophthalmic solution for wetting, cleaning, cushioning, and lubricating contact lenses Adhesion and cushioning ingredient in denture fixatives
Petroleum	Hydrogels as adsorptive pads for catamenial devices and disposable diapers Thickener for bentonite drilling muds Thickener for secondary oil-recovery fluids in waterflooding process
Pharmaceutical	Water-soluble coating for tablets Suspending agent to inhibit settling of ceramic lotion
Printing	Microencapsulation of inks
Soap and detergent	Emollient and thickener for detergent bars and liquids
Textile	Additive to improve dyeability and antistatic properties of polyolefin, polyester, and polyamide fibers

Poly(ethylene oxide) films have been used to produce seed tapes, which consist of seeds sandwiched between two narrow strips of film sealed at the edges. When the seed tape is planted, water from the soil dissolves the water-soluble film within a day or two, releasing the seed for germination. Because the seeds are properly spaced along the tape, the process virtually eliminates the need for thinning of crops.

Films of poly(ethylene oxide) are also used to manufacture water-soluble packages for preweighed quantities of fertilizers, pesticides, insecticides, detergents, dyestuffs, and the like. The packages dissolve quickly in water, releasing the contents. They eliminate the need for weighing and offer protection to the user from toxic or hazardous substances.

Poly(ethylene oxide) forms a water-insoluble association complex with poly(acrylic acid). This is the basis of microencapsulation of nonaqueous printing inks. Dry, free-flowing powders obtained by this process can be used to produce “carbonless” carbon papers (see “Microencapsulation” in [Chapter 5](#)). When pressure is applied to the paper coated with the microencapsulated ink, the capsule wall ruptures and the ink is released.

The formation of a water-insoluble association complex of poly(ethylene oxide) and poly(acrylic acid) is also the basis for a soil stabilization process to prevent erosion of soil on hillsides and river banks.

A variety of different types of adhesives can be produced by forming association complexes of poly(ethylene oxide) with tannin or phenolic resins. Examples include wood glue, water-soluble quickset adhesive, and pressure-sensitive adhesives.

High-molecular-weight poly(ethylene oxide) resins are effective flocculants for many types of clays, coal suspensions, and colloidal silica, and so find application as process aids in mining and hydrometallurgy.

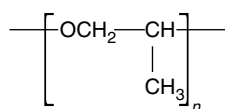
The turbulent flow of water through pipes and hoses or over surfaces causes the effect known as *hydrodynamic drag*. High-molecular-weight poly(ethylene oxide) resins are most effective in reducing the hydrodynamic drag and thus find use in fire fighting, where small concentrations of these resins (50–100 ppm) reduce the pressure loss in fire hoses and make it possible to deliver as much as 60% more water through a standard 2.5-in. (6.35-cm)-diameter fire hose. The Union Carbide product UCAR Rapid Water Additive, which contains high-molecular-weight poly(ethylene oxide) as the active ingredient, is a hydrodynamic-drag-reducing additive for this application.

The ability of poly(ethylene oxide) to reduce hydrodynamic drag has also led to its use in fluid-jet systems used for cutting soft goods, such as textiles, rubber, foam, cardboard, etc. In these systems specially designed nozzles produce a very-small-diameter water jet at a pressure of 30,000–60,000 psi (200–400 MPa). Although a plain water disperses significantly as it leaves the nozzle, with poly(ethylene oxide) addition the stream becomes more cohesive and maintains its very small diameter up to 4 in. (10 cm) from the nozzle.

Chemical or irradiation cross-linking of poly(ethylene oxide) resins yield *hydrogels*, which are not water soluble but water absorptive, capable of absorbing 25–100 times their own weight of water. These hydrogels are reportedly useful in the manufacture of absorptive pads for catamenial devices and disposable diapers.

The water absorbed by the hydrogels is also readily desorbed by drying the hydrogel. This characteristic is the basis for the use of these hydrogels as so-called *soil amendments*. When mixed with ordinary soil in a concentration of about 0.001–5.0 wt% of the soil, these hydrogels will reduce the rate of moisture loss due to evaporation but will still release water to the plants and thus eliminate the need for frequent watering of the soil.

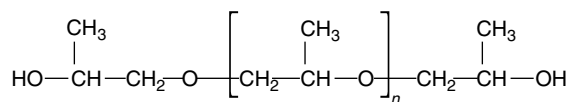
4.3.5.4 Poly(Propylene Oxide)



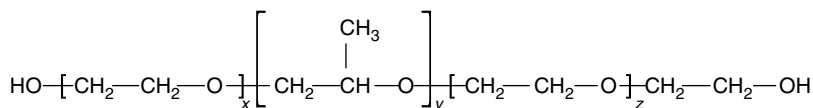
Monomer	Polymerization	Major Uses
Propylene oxide	Base-catalyzed ring-opening polymerization	Polyols for polyurethane foams, surfactants, lubricants cosmetic bases

Propylene oxide is polymerized by methods similar to those described in the preceding section for poly(ethylene oxide). Like the latter, low- and high-molecular-weight polymers are of commercial interest.

Poly(propylene oxide)s of low molecular weight (i.e., from 500 to 3500), often referred to as *polypropylene glycols* (PPGs), are important commercial materials mainly because of their extensive use in the production of polyurethane foams (see [Chapter 2](#) and [Chapter 4](#)). PPGs are less hydrophilic and lower in cost and may be prepared by polymerizing propylene oxide in the presence of propylene glycol as an initiator and sodium hydroxide as a catalyst at about 160°C. The polymers have the general structure



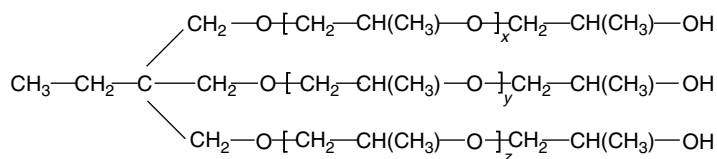
The end hydroxy groups of the polymer are secondary groups and are ordinarily rather unreactive in the urethane reaction. Initially, this limitation was overcome by the preparation of isocyanate-terminated prepolymer and by the use of block copolymers with ethylene oxide. The latter products are known as *tipped polyols* and are terminated with primary hydroxy groups of enhanced activity.



(Note that straight PEG is not satisfactory for polyurethane foam production due to its water sensitivity and tendency to crystallize.)

The later advent of more powerful catalysts, however, made it possible for straight PPG to be used in the preparation of flexible polyurethane foams (see one-shot processes in [Chapter 2](#)) without recourse to the foregoing procedures. Also, today the bulk of the polyethers used are triols rather than diols, since these lead to slightly cross-linked flexible foams with improved load-bearing characteristics.

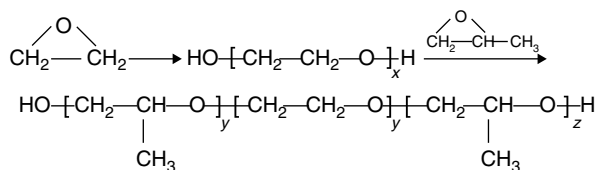
The polyether triols are produced by polymerizing propylene oxide by using 1,1,1-trimethylolpropane, 1,2,6-hexane triol, or glycerol as the initiator. The use of, for example, trimethylolpropane leads to the following polyether triol.



For flexible polyurethane foams, polyether triols of molecular weights from 3000 to 3500 are normally used because they give the best balance of properties. For the production of rigid foams, polyether triols of lower molecular weight (about 500) are used to increase the degree of cross-linking. Alternatively, polyether polyols of higher functionality, such as produced by polymerizing propylene oxide with pentaerythritol or sorbitol, may be used.

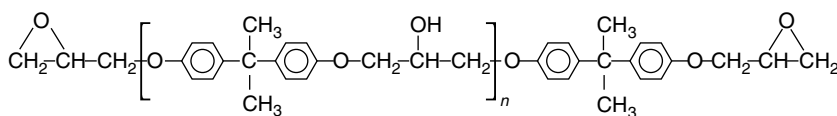
Copolymerization of ethylene oxide and propylene oxide yields quite valuable functional fluids of various sorts. The random copolymers of ethylene and propylene oxides of relatively low molecular weights are water soluble when the proportion of ethylene oxide is at least 40–50% by weight.

The block copolymers consist of sequences of “blocks” of all oxypropylene or all-oxyethylene groups, as shown.



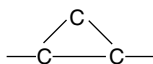
Properties vary considerably, depending on the lengths and arrangements of these blocks. The block copolymers comprise unique and valuable surface-active agents. They can act as breakers for water-in-oil emulsions, as defoamers, and as wetting and dispersing agents.

4.3.5.5 Epoxy Resins



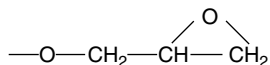
Monomers	Polymerization	Major Uses
Bisphenol A, epichlorohydrin	Condensation and ring-opening polymerization	Surface coating (44%), laminates and composites (18%), moldings (9%), flooring (6%), adhesives (5%)

Epoxide or epoxy resins [14,54,55] contain the epoxide group, also called the epoxy, oxirane, or ethoxyline group, which is a three-membered oxide ring:



(The simplest compound in which the epoxy group is found is ethylene oxide.) In the uncured stage epoxies are polymers with a low degree of polymerization. They are most often used as thermosetting resins which cross-link to form a three-dimensional nonmelting matrix. A curing agent (hardener) is generally used to achieve the cross-linking. In room-temperature curing the hardener is generally an amine such as diethylene triamine or triethylenetetramine. For elevated temperature curing a number of different curing agents could be utilized, including aromatic amines and acid anhydrides.

Epoxy resins first developed commercially and still completely dominating the worldwide markets are those based on 2,2-bis(4'-hydroxyphenyl) propane, more commonly known as bisphenol A (as it is produced by condensation of phenol with acetone) and 1-chloro-2,3-epoxy-propane, also known as epichlorohydrin. It can be seen from the general formula of these resins that the molecular species concerned is a linear polyether with terminal glycidyl ether group



and secondary hydroxyl groups occurring at regular intervals along the length of the macromolecule. The number of repeating units (n) depends essentially on the molar ratio of bisphenol A and epichlorohydrin. When $n=0$, the product is diglycidyl ether and the molecular weight is 340. When $n=10$, the molecular weight is about 3000. Commercial liquid epoxy resins based on bisphenol A and epichlorohydrin have average molecular weights from 340 to 400, and it is therefore obvious that these materials are composed

largely of diglycidyl ether. The liquid resin is thus often referred to as DGEBA (diglycidyl ether of bisphenol A). Similarly, the epoxy resin based on bis(4-hydroxyphenyl)methane, more commonly as bisphenol F (as it is produced by the condensation of phenol with formaldehyde) and epichlorohydrin is referred to as DGEBF.

DGEBA may be reacted with additional quantities of bisphenol A in an advancement reaction. This advancement produces higher-molecular-weight solid resins possessing a higher melting point ($> 90^{\circ}\text{C}$). Advancement generally increases flexibility, improves salt fog corrosion resistance, and increases hydroxyl content, which can be utilized later for cross-linking. Possessing generally low functionality (number of epoxy groups), their major use is in coatings. They provide outstanding adhesion and good salt fog corrosion resistance.

Commercial solid epoxy resins seldom have average molecular weights exceeding 4000, which corresponds to an average value of n of about 13. Resins with molecular weights above 4000 are of limited use since their high viscosity and low solubility make subsequent processing difficult.

4.3.5.5.1 Resin Preparation

The molecular weights of epoxy resins depend on the molar ratio of epichlorohydrin and bisphenol A used in their preparation (see Table 4.25). In a typical process for the production of liquid epoxy resins, epichlorohydrin and bisphenol A in the molar ratio of 10:1 are added to a stainless steel kettle fitted with a powerful anchor stirrer. The water content of the mixture is reduced to below 2% by heating the mixture until the epichlorohydrin–water distills off. After condensation, the epichlorohydrin layer is returned to the kettle, the water being discarded.

When the necessary water content of the reaction mixture is reached, the reaction is started by the slow addition of sodium hydroxide (2 mole per mole of bisphenol A) in the form of 40% aqueous solution, the temperature being maintained at about 100°C . The water content of the reaction mixture should be maintained between 0.31% and 2% by weight throughout the reaction if high yields (90–95%) are to be obtained. (No reaction occurs under anhydrous conditions, and undesired by-products are formed if the water content is greater than 2%). Besides distilling off the water as an azeotrope with the epichlorohydrin, the water content can also be partly controlled by the rate of addition of the caustic soda solution.

When all the alkali has been added, which may take 2–3 h, the excess epichlorohydrin is recovered by distillation at reduced pressure. A solvent such as toluene or methyl isobutyl ketone is then added to the cooled reaction product to dissolve the resin and leave the salt formed in the reaction.

The resin solution is washed with hot water, and after filtration and further washing, the solvent is removed by distillation and the resin is dried by heating under vacuum.

Though the pure diglycidyl ether of bisphenol A is a solid (m.p. 43°C), the commercial grades of the resin which contain a proportion of high-molecular-weight materials are supercooled liquid with viscosities of about 100–140 P at room temperature. The high-molecular-weight epoxy resins usually manufactured have values of n in the general formula ranging from 2 to 12. These resins are synthesized by allowing epichlorohydrin and bisphenol A to interact in the presence of excess sodium hydroxide.

TABLE 4.25 Effect of Reactant Ratio on Molecular Weight of Epoxy Resins

Molar Ratio Epichlorohydrin/Bisphenol A	Molecular Weight	Epoxide Equivalent ^a	Softening Point ($^{\circ}\text{C}$)
10:1	370	192	9
2:1	451	314	43
1.4:1	791	592	84
1.33:1	802	730	90
1.25:1	1133	862	100
1.2:1	1420	1176	112

^a This is the weight of resin (in grams) containing one epoxide equivalent. For a pure diglycidyl ether (mol. wt. 340) with two epoxy groups per molecule, epoxide equivalent = $340/2 = 170$.

In the *taffy process* usually employed, a mixture of bisphenol A and epichlorohydrin (the molar ratio of the reactants used depends on the resin molecular weight required; see Table 4.25) is heated to 100°C and aqueous sodium hydroxide (NaOH–epichlorohydrin molar ratio 1.3:1) is added slowly with vigorous stirring, the reaction being completed in 1–2 h. A white puttylike taffy (which is an emulsion of about 30% water in resin and also contains salt and sodium hydroxide) rises to the top of the reaction mixture. The lower layer of brine is removed; the resinous layer is coagulated and washed with hot water until free from alkali and salt. The resin is then dried by heating and stirring at 150°C under reduced pressure, poured into cooling pans, and subsequently crushed and bagged.

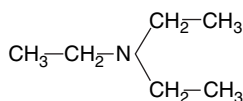
To avoid the difficulty of washing highly viscous materials, higher-molecular-weight epoxy resins may also be prepared by a two-stage process (advancement reaction, described earlier). This process consists of fusing a resin of lower molecular weight with more bisphenol A at about 190°C. The residual base content of the resin is usually sufficient to catalyze the second-stage reaction between the phenolic hydroxyl group and the epoxy group. Typical data of some commercial glycidyl ether resins are given in Table 4.26.

Solid resins have been prepared with narrow molecular-weight distributions. These resins melt sharply to give low-viscosity liquids, which enables incorporation of larger amounts of fillers with a consequent reduction in cost and coefficient of expansion. These resins are therefore useful in casting operations.

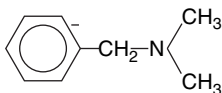
4.3.5.5.2 Curing

To convert the epoxy resins into cross-linked structures, it is necessary to add a curing agent. Most of the curing agents in common use can be classified into three groups: *tertiary amines*, *polyfunctional amines*, and *acid anhydrides*.

Examples of tertiary amines used as curing agents for epoxy resins include:



Triethylamine (TEA)

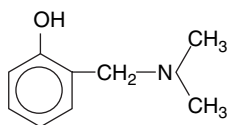


Benzyldimethylamine (BDA)

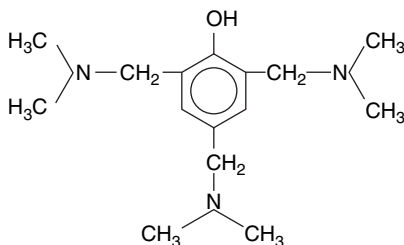
TABLE 4.26 Typical Properties of Some Commercial Glycidyl Ether Resins

Resin	Average Molecular Weight	Epoxide Equivalent	Melting Point (°C)
A	340–400	175–210	—
B	450	225–290	—
C	700	300–375	40–50
D	950	450–525	64–75
E	1400	870–1025	95–105
F	2900	1650–2050	125–132
G	3800	2400–4000	145–155

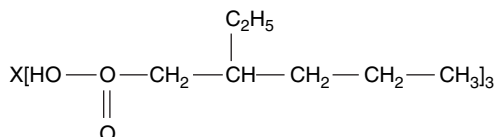
Source: From Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.



Dimethylaminomethylphenol (DMAMP)

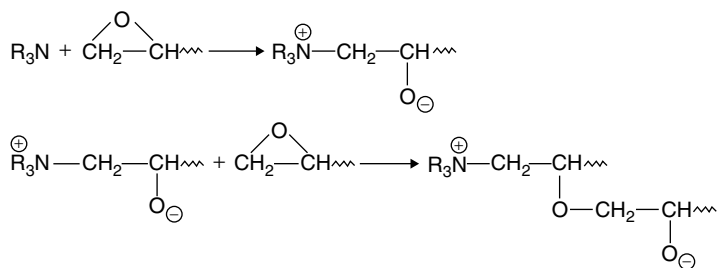


Tri(dimethylaminomethyl) Phenol (TDMAMP)



Tri-2-ethylhexoate salt of TDMAMP (denoted as X)

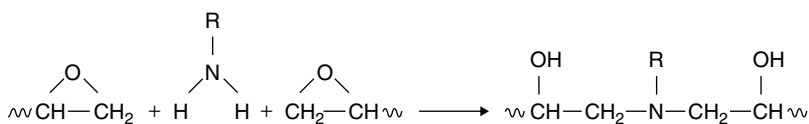
Tertiary amines are commonly referred to as catalytic curing agents since they induce the direct linkage of epoxy groups to one another. The reaction mechanism is believed to be as follows:



Since the reaction may occur at both ends of the diglycidyl ether molecule, a cross-linked structure will be built up. The overall reaction may, however, be more complicated because the epoxy group, particularly when catalyzed, also reacts with hydroxyl groups. Such groups may be present in the higher-molecular-weight homologues of the diglycidyl ether of bisphenol A, or they may be formed as epoxy rings are opened during cure.

In contrast to tertiary amine hardeners, which, as shown, cross-link epoxide resins by a catalytic mechanism, polyfunctional primary and secondary amines act as reactive hardeners and cross-link epoxy resins by bridging across epoxy molecules.

An amine molecule with two active hydrogen atoms can link across two epoxy molecules, as shown:



With polyfunctional aliphatic acid aromatic amines having three or more active hydrogen atoms in amine groups, this type of reaction results in a network polymer (see Figure 1.20). Generally speaking,

aliphatic amines provide fast cures and are effective at room temperature, whereas aromatic amines are somewhat less reactive but give products with higher heat-distortion temperatures. Polyfunctional amines are widely used in adhesive, casting, and laminating applications.

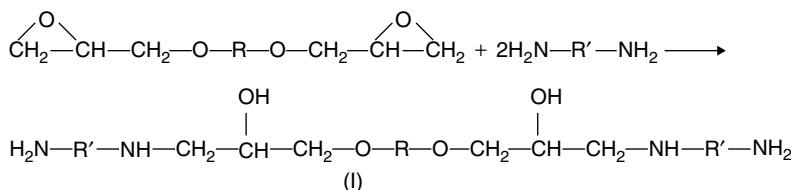
Diethylenetriamine (DETA), $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$, and triethylenetetramine (TETA), $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$, are highly reactive primary aliphatic amines with five and six active hydrogen atoms available for cross-linking, respectively. Both materials will cure (harden) liquid epoxy resins at room temperature and produce highly exothermic reactions.

With DETA the exothermic temperature may reach as high as 250°C in 200-g batches. With this amine used in the stoichiometric quantity of 9–10 pts phr (parts per hundred parts resin), the room temperature pot life is less than an hour. The actual time, however, depends on the ambient temperature and the size of the batch. With TETA, 12–13 pts phr are required.

Dimethylaminopropylamine (DMAPA), $(\text{CH}_3)_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$, and diethylaminopropylamine (DEAPA), $(\text{C}_2\text{H}_5)_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$, are slightly less reactive and give a pot life of about 140 min (for a 500-g batch) and are sometimes preferred. Note that both DMAPA and DEAPA have less than three hydrogen atoms necessary for cross-linking by reaction with epoxy groups.

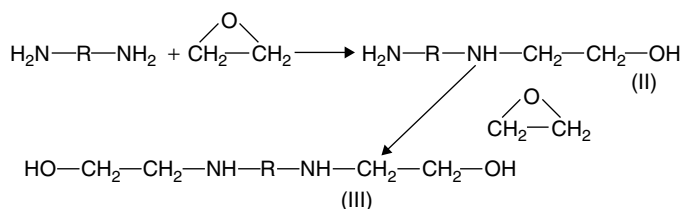
Other examples of amine curing agents with less than three hydrogen atoms are diethanolamine (DEA), $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$, and piperidine (see later). These curing agents operate by means of two-part reaction. Firstly, the active hydrogen atoms of the primary and secondary amine groups are utilized in the manner already described. Thereafter, the resulting tertiary amines, being sufficiently reactive to initiate polymerization of epoxy groups, function as catalytic curing agents, as described previously.

As a class, the amines usually suffer from the disadvantage that they are pungent, toxic, and skin sensitizers. To reduce toxicity, the polyfunctional amines are often used in the form of *adducts*. A number of such modified amines have been introduced commercially. For example, reaction of the amine with a mono- or polyfunctional glycidyl material will give a higher-molecular-weight product with less volatility.



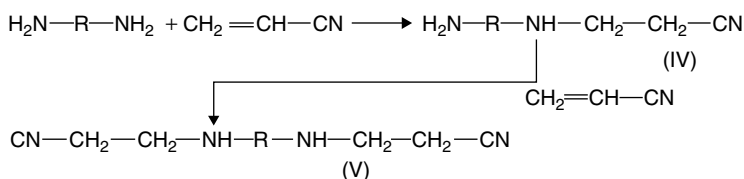
An advantage of such modified amines is that because of higher molecular weight larger quantities are required for curing, and this helps to reduce errors in metering the hardener. These hardeners are also extremely active, and the pot life for a 500-g batch may be as little as 10 min.

The glycidyl adducts are, however, skin irritants, being akin to the parent amines in this respect. Substitution of the hydroxyethyl group and its alkyl and aryl derivatives at the nitrogen atom is effective in reducing the skin sensitization effects of primary aliphatic amines. Both ethylene and propylene oxides have thus been used in the preparation of adducts from a variety of amines, including ethylene diamine and diethylenetriamine.



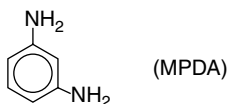
Such adducts from diethylenetriamine appear free of skin sensitizing effects. A hardener consisting of a blend of the reaction products II and III is a low-viscosity liquid giving a pot life (for a 500-g batch) of 16–18 min at room temperature.

Modification of primary amines with acrylonitrile results in hardeners with reduced activity.



Commercial hardeners are mixtures of the addition compounds IV and V. Since accelerating hydroxyl groups are not present in IV and V (in contrast to I, II, and III), these hardeners have reduced activity and so give longer pot lives.

A number of aromatic amines also function as epoxy hardeners. Since they introduce the rigid benzene ring structure into the cross-linked network, the resulting products have significantly higher heat-distortion temperatures than are obtainable with the aliphatic amines (see Table 4.27). For example, metaphenylenediamine (MPDA) (shown below) gives cure resins with a heat distortion temperature of 150°C and very good chemical resistance. The hardener finds use in the manufacture of chemical resistance laminates.



Diaminodiphenylmethane (DAPPM) (below)

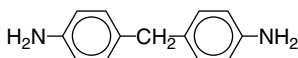


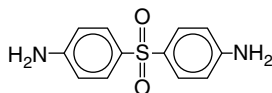
TABLE 4.27 Characteristics of Amine Hardeners Used in Low-Molecular-Weight Bisphenol A-Based Epoxy Resins

Hardener ^a	Parts used per 100 Parts Resin	Pot Life (500-g Batch)	Typical Cure Schedule	Max HDT of Cured Resin (°C)	Applications
DETA	10–11	20 min	Room temperature	110	General purpose
DEAPA	7	140 min	Room temperature	97	General purpose
DETA-glycidyl adduct	25	10 min	Room temperature	75	Adhesive laminating, fast cure
DETA-ethylene oxide adduct	20	16 min	Room temperature	92	—
MPDA	14–15	6 h	4–6 h at 150°C	150	Laminates, chemical resistance
DADPM	28.5	—	4–6 h at 165°C	160	Laminates
DADPS	30	—	8 h at 160°C	175	Laminates
Piperidine	5–7	8 h	3 h at 100°C	75	General purpose
Triethylamine	10	7 h	Room temperature	—	Adhesives
BDA	15	75 min	Room temperature	—	Adhesives
TDMAMP	6	30 min	Room temperature	64	Adhesives, coatings
2-Ethyl hexoate salt of TDMAMP	10–14	3–6 h	—	—	Encapsulation

^a For chemical formulas see text.

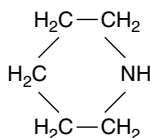
Source: From Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.

and diaminodiphenyl sulfone (DADPS) (below)



used in conjunction with an accelerator provide even higher heat-distortion temperatures but at some expense to chemical resistance.

Piperidine, a cyclic aliphatic amine



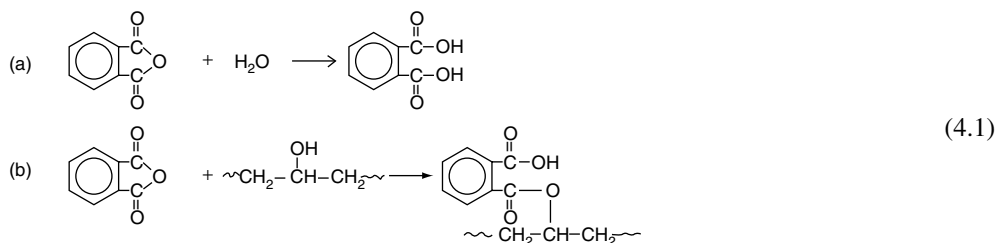
has been in use as an epoxy hardener since the early patents of Castan. Although a skin irritant, this hardener is still used for casting larger masses than are possible with primary aliphatic amines. Note that because it has only one active hydrogen atom in the amine group, piperidine operates by a two-part reaction in curing. Typical amine hardeners and their characteristics are summarized in [Table 4.27](#).

Cyclic acid anhydrides are widely employed as curing agents for epoxy resins. Compared with amines they are less skin sensitive and generally give lower exotherms in curing reaction. Some acid curing agents provide cured resins with very high heat-distortion temperatures and with generally good mechanical, electrical, and chemical properties. The acid-cured resins, however, show less alkali resistance than amine-cured resins because of the susceptibility of ester groups to hydrolysis. Anhydride curing agents find use in most of the important applications of epoxy resins, particularly in casting and laminates.

In practice, acid anhydrides are preferred to acids since the latter are generally less soluble in the resin and also release more water on cure, leading to foaming of the product. Care must be taken, however, during storage since the anhydrides in general are somewhat hygroscopic. Examples of some anhydrides which are used are shown in [Figure 4.35](#).

The mechanism of hardening by anhydride is complex. In general, however, two types of reactions occur: (1) opening of the anhydride ring with the formation of carboxy groups, and (2) opening of the epoxy ring. The most important reactions which may occur are shown in what follows, with phthalic anhydride as an example.

1. The first stage of the interaction between an acid anhydride and an epoxy resin is believed to be the opening of the anhydride ring by (a) water (traces of which may be present in the system) or (b) hydroxy groups (which may be present as pendant groups in the original resin or may result from reaction (2a)).



2. The epoxy ring may then be opened by reaction with (a) carboxylic groups formed by reactions (1a, b) or (b) hydroxyl groups [see (1)].

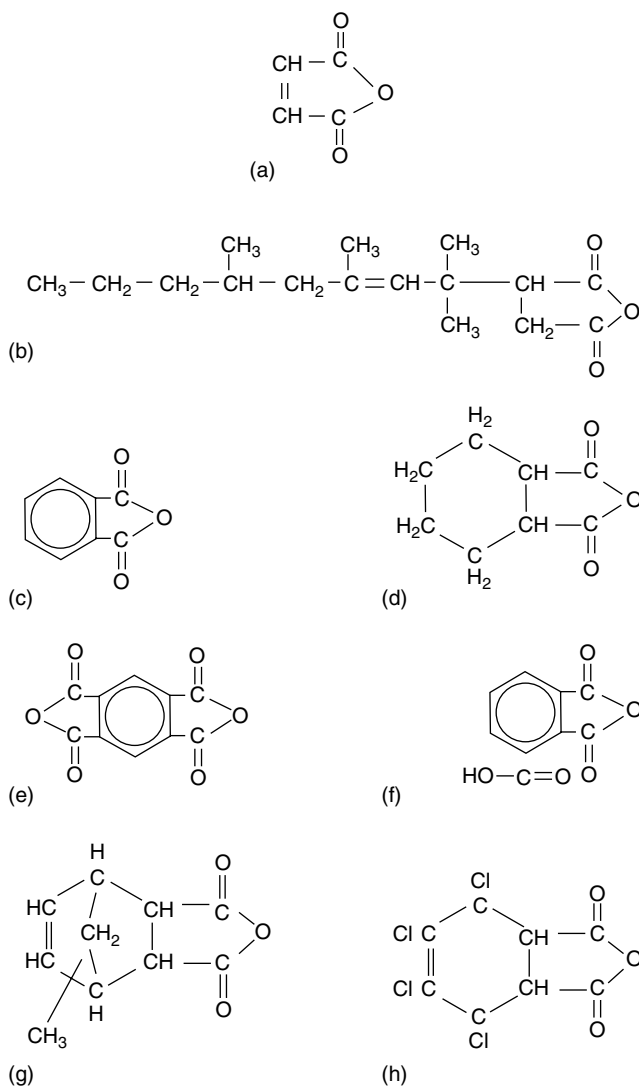
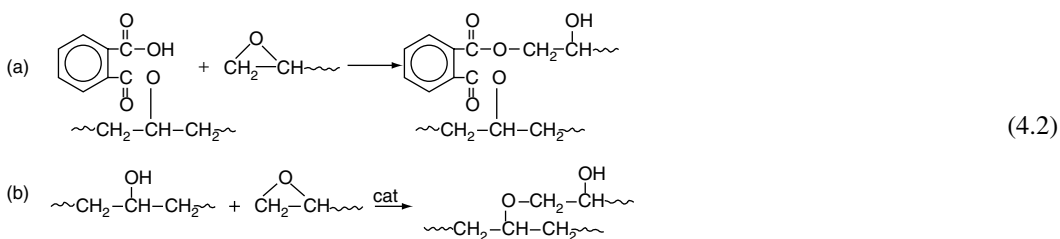
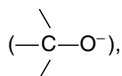


FIGURE 4.35 Anhydride curing agents. (a) Maleic anhydride. (b) Dodecenylsuccinic anhydride. (c) Phthalic anhydride. (d) Hexahydrophthalic anhydride. (e) Pyromellitic anhydride. (f) Trimellitic anhydride. (g) Nadic methyl anhydride. (h) Chlorendic anhydride.



The reaction between an epoxy resin and an anhydride is rather sluggish. In commercial practice, the curing is accelerated by the use of organic bases to catalyze the reaction. These are usually tertiary amines such as α -methylbenzyl-dimethylamine and butylamine. The tertiary amine appears to react

preferentially with the anhydride to generate a carboxy anion ($-\text{COO}^-$). This anion then opens an epoxy ring to give an alkoxide ion



which forms another carboxy anion from a second anhydride molecule, and so on.

Phthalic anhydride is the cheapest anhydride curing agent, but it has the disadvantage of being rather difficult to mix with the resin. Liquid anhydrides (e.g., dodecenylsuccinic anhydride and nadic methyl anhydride), low-melting anhydrides (e.g., hexahydrophthalic anhydride), and eutectic mixtures are more easily incorporated into the resin. Since maleic anhydride produces brittle products, it is seldom used by itself and is used as a secondary hardener in admixture with other anhydrides. Dodecenylsuccinic anhydride imparts flexibility into the casting, whereas chlorendic anhydride confers flame resistance.

Anhydride-cured resins generally have better thermal stability. Pyromellitic dianhydride with higher functionality produces tightly cross-linked products of high heat-distortion temperatures. Heat-distortion temperatures as high as 290°C have been quoted. Table 4.28 summarizes the characteristics of some of the anhydride hardeners.

In addition to the amine and anhydride hardeners, many other curing agents have been made available. Among them are the so-called fatty polyamides. These polymers are of low molecular weight (2000–5000) and are prepared by treating dimer acid (which is a complex mixture consisting of 60–75% dimerized fatty acids together with lesser amounts of trimerized acids and higher polymers) with stoichiometric excess of ethylenediamine or diethylenetriamine so that the resultant amides have free amine groups.

Fatty polyamides are used to cure epoxy resins where a more flexible product is required, particularly in adhesive and coating applications. An advantage of the system is that roughly similar quantities of hardener and resin are required and, because it is not critical, metering can be done visually without the need of measuring aids. They thus form the basis of some domestic adhesive systems.

Also used with epoxy resins for adhesives is dicyanodiamide, $\text{H}_2\text{N}-\text{C}(=\text{NH})\text{NH}-\text{CN}$. It is insoluble in common resins at room temperature but is soluble at elevated temperatures and thus forms the basis of a one-pack system.

4.3.5.5.3 Other Epoxies

Resins containing the glycidyl ether group

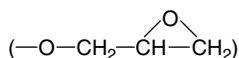


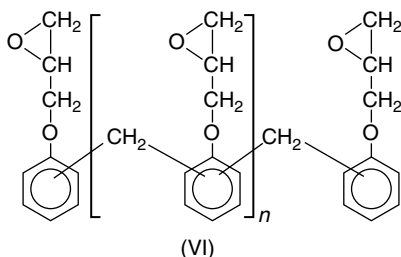
TABLE 4.28 Properties of Some Anhydride Hardeners used in Low-Molecular-Weight Bisphenol A-Based Epoxy Resins

Hardener (Anhydride)	Parts used per 100 Parts Resin	Typical Cure Schedule	Max HDT of Cured Resin (°C)	Application
Phthalic	35–45	24 h at 120°C	110	Casting
Hexahydrophthalic (+ accelerator)	80	24 h at 120°C	130	Casting
Pyromellitic	26	20 h at 220°C	290	High HDT
Nadic methyl	80	16 h at 120°C	202	High HDT
Dodecenylsuccinic (+ accelerator)		2 h at 100°C + 2 h at 150°C	38	Flexibilizing
Chlorendic	100	24 h at 180°C	180	Flame retarding

Source: From Brydson, J. A. 1982. *Plastics Materials*. Butterworth Scientific, London, UK.

result from the reaction of epichlorohydrin and hydroxy compounds. Although bisphenol A is the most commonly used hydroxyl compound, a few glycidyl ether resins based on other hydroxy compound are also commercially available, including novolac epoxies, polyglycol epoxies, and halogenated epoxies.

A typical commercial novolac epoxy resin (VI) produced by epoxidation of phenolic hydroxyl groups of novolac (see the section on phenolformaldehyde resins) by treatment with epichlorohydrin has an

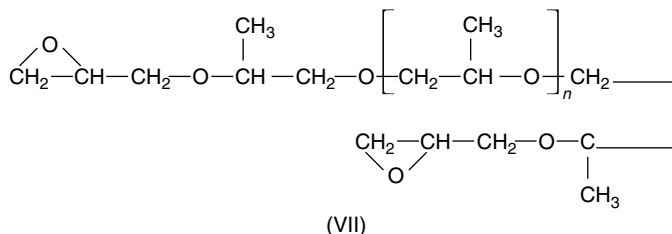


(VI)

average molecular weight of 650 and contains about 3.6 epoxy groups per molecule.

Because of higher functionality, the novolac epoxy resins give, on curing, more highly cross-linked products than the bisphenol A-based resins. This results in greater thermal stability, higher heat-deflection temperatures, and improved chemical resistance. Their main applications have been in high-temperature adhesives, heat-resistant structural laminates, electrical laminates resistant to solder baths, and chemical-resistant filament-wound pipes. The use of novolac epoxies has been limited, however, by their high viscosity and consequent handling difficulties.

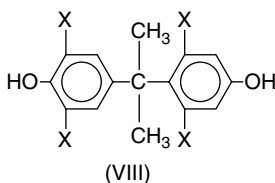
Polymeric glycols such as polypropylene glycol may be epoxidized through the terminal hydroxy groups to give diglycidyl ethers (VII).



(VII)

In commercial products n usually varies from 1 to 6. Alone, these resins give soft products of low strength on curing. So they are normally used in blends with bisphenol A- or novolac-based resins. Added to the extent of 10–30%, they improve resilience without too large a loss in strength and are used in such applications as adhesives and encapsulations.

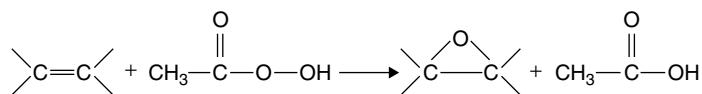
Epoxies containing halogens have flame-retardant properties and may be prepared from halogenated hydroxy compounds. Halogenated epoxies are available based on tetrabromobisphenol A and tetrachlorobisphenol A (VIII).



(VIII)

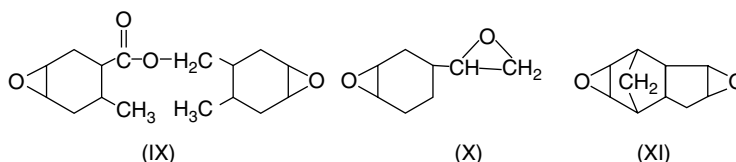
The brominated resins are more effective than the chlorinated resins and have become more predominant commercially. The ability of the resins to retard or extinguish burning is due to the evolution of hydrogen halide at elevated temperatures. Brominated epoxy resins are generally blended with other epoxy resins to impart flame retardance in such applications as laminates and adhesives.

Nonglycidyl ether epoxy resins are usually prepared by treating unsaturated compounds with peracetic acid.



Two types of nonglycidyl ether epoxy resins are commercially available: cyclic aliphatic epoxies and acyclic aliphatic epoxies.

Cyclic aliphatic epoxy resins were first introduced in the United States. Some typical examples of commercial materials are 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate (Unox epoxide 201, liquid) (IX), vinylcyclohexene dioxide (Unox epoxide 206, liquid) (X), and dicyclopentadiene dioxide (Unox epoxide 207, solid) (XI).



Generally, acid anhydrides are the preferred curing agents since amines are less effective. A hydroxy compound, such as ethylene glycol, is often added as initiator.

Because of their more compact structure, cycloaliphatic resins produce greater density of cross-links in the cured products than bisphenol A-based glycidyl resins. This generally leads to higher heat-distortion temperatures and to increased brittleness.

The products also are clearly superior in arc resistance and are track resistant. Thus although bisphenol A-based epoxies decompose in the presence of a high-temperature arc to produce carbon which leads to tracking and insulation failure, cycloaliphatic epoxies oxidize to volatile products which do not cause tracking. This has led to such applications as heavy-duty electrical castings and laminates, tension insulators, rocket motor cases, and transformer encapsulation.

Acyclic aliphatic resins differ from cyclic aliphatic resins in that the basic structure of the molecules in the former is a long chain, whereas the latter, as shown, contains ring structures. Two types of acyclic aliphatic epoxies are commercially available, namely, epoxidized diene polymers and epoxidized oils.

Typical of the epoxidized diene polymers are the products produced by treatment of polybutadiene with peracetic acid. Epoxidized diene polymers are not very reactive toward amines but may be cross-linked with acid hardeners. Cured resins have substantially higher heat-distortion temperatures (typically, 250°C) than do the conventional amine-cured diglycidylether resins.

Epoxidized oils are obtained by treatment of drying and semidrying oils (unsaturated), such as linseed and soybean oils, with peracetic acid. Epoxidized oils find use primarily as plasticizers and stabilizers for PVC.

4.3.5.5.4 Applications

Epoxy resins have found a wide range of applications and a steady rate of growth over the years mainly because of their versatility. Properties of the cured products can be tailored by proper selection of resin, modifier, cross-linking agent, and the curing schedule.

The main attributes of properly cured epoxy systems are outstanding adhesion to a wide variety of substrates, including metals and concrete; ability to cure over a wide temperature range; very low shrinkage on cure; excellent resistance to chemicals and corrosion; excellent electrical insulation properties; and high tensile, compressive, and flexural strengths.

In general, the toughness, adhesion, chemical resistance, and corrosion resistance of epoxies suit them for protective coating applications. It is not surprising that about 50% of epoxy resins are used in protective coating applications.

Two types of epoxy coatings are formulated: those cured at ambient temperature and those that are heat cured. The first type uses amine hardening systems, fatty acid polyamides, and polymercaptans as

curing agents. Very high cure rates may be achieved by using mercaptans. Heat-cured types use acid anhydrides and polycarboxylic acids as well as formaldehyde resins as curing agents.

Typical coating applications for phenol-formaldehyde resin-modified epoxies include food and beverage can coatings, drum and tank liners, internal coatings for pipes, wire coating, and impregnation varnishes. Ureaformaldehyde resin-modified epoxies offer better color range and are used as appliance primers, can linings, and coatings for hospital and laboratory furniture.

Environmental concerns have prompted major developmental trends in epoxy coating systems. Thus epoxy coating systems have been developed to meet the high-temperature and hot-acid environments to which SO₂ scrubbers and related equipment are subjected. Ambient curable epoxy systems have been developed to provide resistance to concentrated inorganic acids.

In the development of maintenance and marine coatings, the emphasis has been on the development of low-solvent, or solvent-free, coatings to satisfy EPA volatile organic content standards. Thus liquid epoxy systems based on polyamidamines have been developed. Epoxies have also been formulated as powdered coatings, thus completely eliminating solvents.

Pipe coatings still represent a major market for epoxies. High-molecular-weight powdered formulations are used in this application.

The important maintenance coating area, particularly for pipe and tank coatings, is served by epoxy systems cured with polyamine or polyamidamines. Two-component, air-dried, solventless systems used in maintenance coatings provide tough, durable, nonporous surfaces with good resistance to water, acids, alkalies, organic solvents, and corrosion.

Emulsifiable epoxies of varying molecular weights, water-dilutable modified epoxies, and dispersions of standard resins represent promising developments for coating applications. Can coatings are an important waterborne resin application. Two-component waterborne systems are also finding use as architectural coatings.

For electrical and electronic applications epoxy formulations are available with low or high viscosity, unfilled or filled, slow or fast curing at low or high temperatures. Potting, encapsulation, and casting of transistors, integrated circuits, switches, coils, and insulators are a few electrical applications of epoxies. With their adhesion to glass, electrical properties, and flexural strength, epoxies provide high-quality printed circuit boards. Epoxies have been successfully used in Europe for outdoor insulators, switchgear, and transformers for many years. In these heavy electrical applications, the advantage of cycloaliphatic epoxies over porcelain has been demonstrated.

In a relatively new development, epoxy photopolymers have been used as solder masks and photoresists in printed circuit board fabrications.

Adhesion properties of epoxies, complete reactivity with no volatiles during cure, and minimal shrinkage make the materials outstanding for adhesives, particularly in structural applications. The most commonly known adhesive applications involve the two-component liquids or pastes, which cure at room or elevated temperatures.

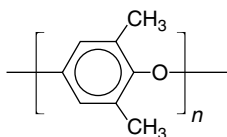
A novel, latent curing system, which gives more than one year pot life at room temperature, has increased the use of epoxies for specialty adhesives and sealants, and for vinyl plastisols. The one-pack system provides fast cure when heated—for example 5 min at 100°C.

Epoxies are used in fiber-reinforced composites, providing high strength-to-weight ratios and good thermal and electrical properties. Filament-wound epoxy composites are used for rocket motor casings, pressure vessels, and tanks. Glass-fiber reinforced epoxy pipes are used in the oil, gas, mining, and chemical industries.

Sand-filled epoxies are used in industrial flooring. Resistance to a wide variety of chemicals and solvents and adhesion to concrete are key properties responsible for this use. Epoxies are also used in patching concrete highways.

Decorative flooring and exposed aggregate systems make use of epoxies because of their low curing shrinkage, and the good bonding of glass, marble, and quartz chip by the epoxy matrix.

4.3.5.6 Poly(Phenylene Oxide)



Monomer	Polymerization	Major Uses
2,6-Dimethylphenol	Condensation polymerization by oxidative coupling	Automotive, appliances, business machine cases, electrical components

Poly(2,6-dimethyl-1,4-phenylene oxide), commonly called poly(phenylene oxide) or PPO, was introduced commercially in 1964. PPO is manufactured by oxidation of 2,6-dimethyl phenol in solution using cuprous chloride and pyridine as catalyst. The monomer is obtained by the alkylation of phenol with methanol. End-group stabilization with acetic anhydride improves the oxidation resistance of PPO.

PPO is counted as one of the engineering plastics. The rigid structure of the polymer molecules leads to a material with a high T_g of 208°C. It is characterized by high tensile strength, stiffness, impact strength, and creep resistance, and low coefficient of thermal expansion. These properties are maintained over a broad temperature range (−45°C to 120°C). One particular feature of PPO is its exceptional dimensional stability among the so-called engineering plastics. The polymer is self-extinguishing.

PPO has excellent resistance to most aqueous reagents and is unaffected by acids, alkalis, and detergents. The polymer has outstanding hydrolytic stability and has one of the lowest water absorption rates among the engineering thermoplastics. PPO is soluble in aromatic hydrocarbons and chlorinate solvents. Several aliphatic hydrocarbons cause environmental stress cracking.

PPO has low molding shrinkage. The polymer is used for the injection molding of such items as pump components, domestic appliance and business machines, and electrical parts such as connectors and terminal blocks.

The high price of PPO has greatly restricted its application and has led to the introduction of the related and cheaper thermoplastic materials in 1966 under the trade name Noryl by General Electric. If PPO ($T_g = 208^\circ\text{C}$) is blended with polystyrene ($T_g \sim 90^\circ\text{C}$) in equal quantities, a transparent polymer is obtained with a single T_g of about 150°C, which apparently indicates a molecular level of mixing. Noryl thermoplastics may be considered as being derived from such polystyrene–PPO blends. Since the electrical properties of the two polymers are very similar, the blends also have similar electrical characteristics. In addition to Noryl blends produced by General Electric, grafts of styrene onto PPO are also available (Xyron by Asahi-Dow).

The styrenic component in polystyrene–PPO blends may not necessarily be straight polystyrene (PS) but instead high-impact polystyrene (HIPS) or some other related material. The most widely used blend is the blend of PPO and HIPS.

Like polystyrene, these blends have the following useful characteristics: (1) good dimensional stability and low molding shrinkage, thus allowing close dimensional tolerance in the production of moldings; (2) low water absorption; (3) excellent resistance to hydrolysis; and (4) very good dielectric properties over a wide range of temperature. In addition, unlike polystyrene, the blends have heat-distortion temperatures above the boiling point of water, and in some grades this is as high as 160°C.

The range of Noryl blends available comprises a broad spectrum of materials superior in many respects, particularly heat deformation resistance, to the general purpose thermoplastics but at a lower price than the more heat resistant materials such as polycarbonates, polyphenylene sulfides, and polysulfones (discussed later). The materials that come close to them in properties are the

ABS/polycarbonate blends. Noryl is also characterized by high dielectric strength (192 V/mil) and low dissipation factors (4.7×10^{-3} at 100 Hz and 3.9×10^{-3} at 10^6 Hz).

In common with other engineering thermoplastics, there are four main groups of modified PPOs available. They are: (1) non-self-extinguishing grades with a heat-distortion temperature in the range 110–106°C and with a notched Izod impact strength at 200–500 J/m; (2) self-extinguishing grades with slightly lower heat-distortion temperatures and impact strengths; (3) non-self-extinguishing glass-reinforced grades (10%, 20%, 30% glass fiber) with heat-distortion temperatures in the range of 120–140°C; and (4) self-extinguishing glass-reinforced grades. Among the special grades that should be mentioned are those containing blowing agents for use in the manufacture of structural foams (see [Chapter 2](#)).

Noryls maybe extruded, injection molded, and blow-molded without undue difficulty. Processing conditions depend on the grade used but in injection molding a typical melt temperature would be in the range 250–300°C.

The introduction of self-extinguishing, glass-reinforced, and structural foam grades has led to steady increase in the use of these materials in five main application areas. These are (1) the automotive industry; (2) the electrical industry; (3) radio and television; (4) business machines and computer housings; and (5) pumps and other plumbing applications.

Use in the automotive industries largely arises from the availability of high impact grades with heat-distortion temperatures above those of the general purpose thermoplastics. Specific uses include instrument panels, steering column cladding, central consoles, loudspeaker housings, ventilator grilles and nozzles, and parcel shelves. In cooling systems, glass-reinforced grades have been used for radiator and expansion tanks. Several components of car heating systems are also produced from modified PPOs. The materials have been increasingly used for car exterior trim such as air inlet and outlet grills and outer mirror housings.

In the electrical industry, well-known applications include fuse boxes, switch cabinets, housing for small motors, transformers, and protective circuits.

Uses in radio and television arise largely from the ability to produce components with a high level of dimensional accuracy coupled with good dielectric properties, high heat-distortion temperatures, and the availability of self-extinguishing grades. Specific uses include coil formers, picture tube deflection yokes, and insert card mountings.

In the manufacture of business machine and computer housings, structural foam grades have found use and moldings weighing as much as 50 kg have been reported. Glass-reinforced grades have widely replaced metals in pumps and other functional parts in washing equipment and central heating systems.

Another PPO, called PPE, is produced by the oxidative coupling of a mixture of 2,6-dimethylphenol and 2,3,6-trimethylphenol. This stiff polymer, like Noryl, is available from General Electric. It is usually modified by blending with PS or HIPS.

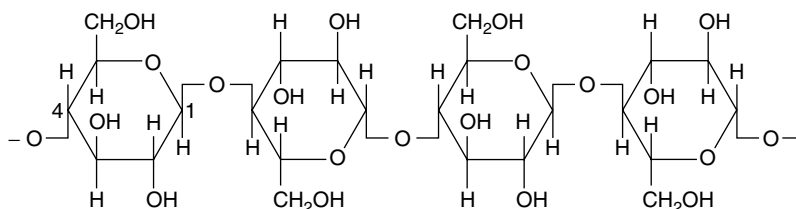
Blends of PPO and polyamide (PA, nylon) are incompatible but good properties can be obtained through the use of compatibilizing agents. The PPO is dispersed in a continuous nylon matrix in these blends. Because of the incompatibility of the two phases, the modulus decreases very little at the T_g of PA (71°C) and is maintained up to the T_g of the PPO phase (208°C).

The PPO–PA blends, which are sold by General Electric under the trade name Noryl GTX, can be baked and painted at 190°C without noticeable warpage or distortion, and have been used for producing automobile fenders.

The PPO–PA blends shown a mold shrinkage of 0.001 in./in. The molding pressure in 15×10^3 lbf/in.² (103 MPa) and the processing temperature 260°C. The heat-deflection temperature of the molded specimen under flexural load of 264 lbf/in.² is typically 190°C and the maximum resistance to continuous heat is 175°C. The coefficient of linear expansion is 10^{-5} cm/cm °C. The mechanical properties of the PPO–PA blends are shown in [Table 4.29](#).

4.3.6 Cellulosic Polymers

Cellulose is a carbohydrate with molecular formula $(C_6H_{10}O_5)_n$, where n is a few thousand. Complete hydrolysis of cellulose by boiling with concentrated hydrochloric acid yields D-glucose, $C_6H_{12}O_6$, in 95–96% yield [56]. Cellulose can thus be considered chemically as a polyanhydroglucose. The structure of cellulose is



The regularity of the cellulose chain and extensive hydrogen bonding between hydroxyl groups of adjacent chains cause cellulose to be a tightly packed crystalline material which is insoluble and infusible. As a result, cellulose cannot be processed in the melt or in solution. However, cellulose derivatives in which there is less hydrogen bonding are processable.

The most common means of preparing processable cellulose derivatives are esterification and etherification of the hydroxyl groups. In the following, the more important commercial cellulosic polymers are described.

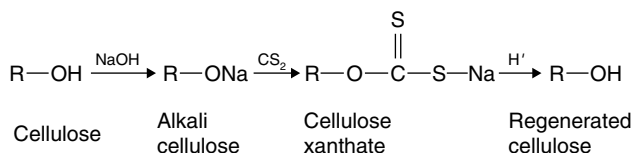
4.3.6.1 Regenerated Cellulose

As mentioned, many derivatives of cellulose are soluble, though cellulose itself is insoluble. A solution of a cellulose derivative can be processed (usually by extrusion) to produce the desired shape (commonly fiber or film) and then treated to remove the modifying groups to reform or regenerated unmodified cellulose. Such material is known as *regenerated cellulose*.

Modern methods of producing regenerated cellulose can be traced to the discovery in 1892 by Cross, Bevan, and Beadle that cellulose can be rendered soluble by xanthate formation by treatment with sodium hydroxide and carbon disulfide and regenerated by acidification of the xanthate solution. This process is known as the *viscose process*. The reactions can be indicated schematically as

TABLE 4.29 Properties of Typical PPO–PA Blends (Noryl GTX 810)

Property	Value
Tensile strength	
10^3 lbf/in. ²	13
MPa	90
Tensile modulus	
10^5 lbf/in. ²	2.0
GPa	1.4
Elongation at break (%)	10
Flexural strength	
10^3 lbf/in. ²	19
MPa	131
Flexural modulus	
10^5 lbf/in. ²	2.25
GPa	1.6
Impact strength, notched Izod	
ft.-lb/in.	1.5
J/m	80



The viscose process is used for the production of textile fibers, known as *viscose rayon*, and transparent packaging film, known as *cellophane* (the name is coined from *cellulose* and *diaphane*, which is French for transparent).

A suitably aged solution of cellulose xanthate, known as *viscose*, is fed through spinnerets with many small holes (in the production of fiber), through a slot die (in the production of film), or through a ring die (in the production of continuous tube used as sausage casing) into a bath containing 10–15% sulfuric acid and 10–20% sodium sulfate at 35–40°C, which coagulates and completely hydrolyzes the viscose. Cellulose is thus regenerated in the desired shape and form.

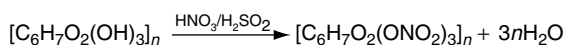
It is possible to carry out a drawing operation on the fiber as it passes through the coagulating bath. The stretching (50–150%) produces crystalline orientation in the fiber. The product, known as *high-tenacity rayon*, has high strength and low elongation and is used in such application as tire cord and conveyor belting.

For the production of cellophane, the regenerated cellulose film is washed, bleached, plasticized with ethylene glycol or glycerol, and then dried; sometimes a coating of pyroxylin (cellulose nitrate solution) containing dibutyl phthalate as plasticizer is applied to give heat sealability and lower moisture permeability.

Cellophane has been extensively and successfully used as a wrapping material, particularly in the food and tobacco industries. However, the advent of polypropylene in the early 1960s has produced a serious competitor to this material.

4.3.6.2 Cellulose Nitrate

Cellulose nitrate or nitrocellulose (as it is often erroneously called) is the doyen of cellulose ester polymers. It is prepared by direct nitration with nitric and sulfuric acid mixtures at about 30–40°C for 20–60 min. Complete substitution at all three hydroxyl groups on the repeating anhydroglucose unit will give cellulose trinitrate containing 14.14% nitrogen:



This material is explosive and is not made commercially, but products with lower degrees of nitration are of importance. The degree of nitration may be regulated by the choice of reaction conditions.

Industrial nitrocelluloses have a degree of substitution somewhere between 1.9 and 2.7 and are generally characterized for their various uses by their nitrogen content, usually about 11% for plastics, 12% for lacquer and cement base, and 13% for explosives.

The largest use of cellulose nitrate is as a base for lacquers and cements. Butyl acetate is used as a solvent. Plasticizers such as dibutyl phthalate and tritolyl phosphate are necessary to give films of acceptable flexibility and adhesion.

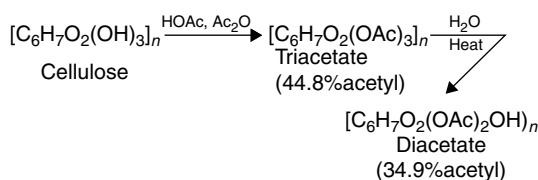
For use as plastic in bulk form, cellulose nitrate is plasticized with camphor. The product is known as *celluloid*. In a typical process alcohol-wet cellulose nitrate is kneaded at about 40°C with camphor (about 30%) to form a viscous plastic mass. Pigments or dyes may be added at this stage. The dough is then heated at about 80°C on milling rolls until the alcohol content is reduced to about 15%.

The milled product is calendered into sheets about 1/2-in. (1.25-cm) thick. A number of sheets are laid up in a press and consolidated into a block. The block is sliced into sheets of thickness 0.005–1 in. (0.012–2.5 cm), which are then allowed to season for several days at about 50°C so that the volatile content is reduced to about 2%. Celluloid sheet and block may be machined with little difficulty if care is taken to avoid overheating.

The high inflammability and relatively poor chemical resistance of celluloid severely restrict its use in industrial applications. Consequently the material is used because of its desirable characteristics, which include rigidity, dimensional stability, low water absorption, reasonable toughness, after-shrinkage around inserts, and ability of forming highly attractive colored sheeting. Today the principal outlets of celluloid are knife handles, table-tennis balls, and spectacle frames. Celluloid is marketed as Xylonite (BX Plastics Ltd.) in UK.

4.3.6.3 Cellulose Acetate

The acetylation of cellulose is usually carried out with acetic anhydride in the presence of sulfuric acid as catalyst. It is not practicable to stop acetylation short of the essentially completely esterified triacetate. Products of lower acetyl content are thus produced by partial hydrolysis of the triacetate to remove some of the acetyl groups:



Cellulose triacetate is often known as *primary cellulose acetate*, and partially hydrolyzed material is called *secondary cellulose acetate*. Many physical and chemical properties of cellulose acetylation products are strongly dependent on the degree of esterification, which is measured by the acetyl content (i.e., the weight of acetyl radical ($\text{CH}_3\text{CO}-$) in the material) or acetic acid yield (i.e., the weight of acetic acid produced by complete hydrolysis of the ester).

The commercial products can be broadly distinguished as cellulose acetate (37–40% acetyl), high-acetyl cellulose acetate (40–42% acetyl), and cellulose triacetate (43.7–44.8% acetyl).

Cellulose acetate containing 37–40% acetyl is usually preferred for use in general-purpose injection-molding compounds. Cellulose acetate, however, decomposes below its softening point, and it is necessary to add a plasticizer (e.g., dimethyl phthalate or triphenyl phosphate), usually 25–35%, to obtain a moldable material. The use of cellulose acetate for molding and extrusion is now small owing largely to the competition of polystyrene and other polyolefins. At the present time the major outlets of cellulose acetate are in the fancy goods trade as toothbrushes, combs, hair slides, etc.

Cellulose acetate with a slightly higher degree of esterification (38.7–40.1% acetyl) is usually preferred for the preparation of fibers, films, and lacquers because of the greater water resistance. A significant application of cellulose acetate film has been found in sea-water desalination by reverse osmosis.

High-acetyl cellulose acetate (40–42% acetyl) has found occasional use in injection-molding compounds where greater dimensional stability is required. However, processing is more difficult.

Cellulose triacetate (43.7–44.8% acetyl) finds little use in molding compositions because its very high softening temperature is not greatly reduced by plasticizers. It is therefore processed in solution. A mixture of methylene chloride and methanol is the commonly used solvent.

The sheeting and fibers are made from cellulose triacetate by casting or by extruding a viscous solution and evaporating the solvent. The sheeting and film are grainless, have good gauge uniformity, and good optical clarity. The products have good dimensional stability and are highly resistant to water, grease, oils, and most common solvents such as alcohol and acetone. They also have good heat resistance and high dielectric constant.

Sheeting and films of cellulose triacetate are used in the production of visual aids, graphic arts, greeting cards, photographic albums, and protective folders. Cellulose triacetate is extensively used for photographic, x-ray, and cinematographic films. In these applications cellulose triacetate has displaced celluloid mainly because the triacetate does not have the great inflammability of celluloid.

4.3.6.4 Other Cellulose Esters

Homologues of acetic acid have been employed to make other cellulose esters. Of these, cellulose propionate, cellulose acetate-propionate, and cellulose acetate-butyrate are produced on a commercial scale. They are produced in a manner similar to that described previously for cellulose acetate. The propionate and butyrate esters are made by substituting propionic acid and propionic anhydride or butyric acid and butyric anhydride for some of the acetic acid and acetic anhydride.

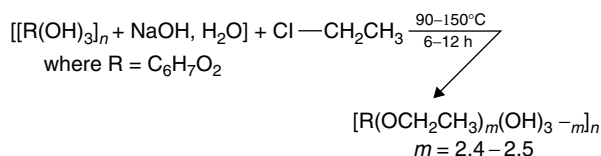
Cellulose acetate-butyrate (CAB) has several advantages in properties over cellulose acetate: lower moisture absorption, greater solubility and compatibility with plasticizer, higher impact strength, and excellent dimensional stability. CAB used in plastics has about 13% acetyl and 37% butyryl content. It is an excellent injection-molding material (Tenite Butyrate by Kodak, Cellidor B by Bayer).

Principal end products of CAB have been for tabulator keys, automobile parts, toys, pen and pencil barrels, steering wheels, and tool handles. In the United States CAB has been used for telephone housings, and extruded CAB piping has been used for conveying water, oil, and natural gas. CAB sheet is readily vacuum formed and is especially useful for laminating with thin-gauge aluminum foil. It also serves particularly well for vacuum metallizing.

Cellulose propionate (Forticel by Celanese) is very similar in both cost and properties to CAB. It has been used for similar purposes as CAB. Cellulose acetate propionate (Tenite Propionate by Kodak) is similar to cellulose propionate. It finds wide use in blister packages and formed containers, safety goggles, motor covers, metallized flash cubes, brush handles, steering wheels, face shields, displays, and lighting fixtures.

4.3.6.5 Cellulose Ethers

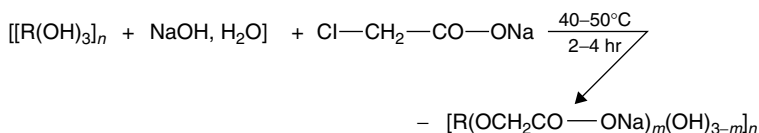
Of cellulose ethers only ethyl cellulose has found application as a molding material. Methyl cellulose, hydroxyethyl cellulose, and sodium carboxymethyl cellulose are useful water-soluble polymers. The first step in the manufacture of each of these materials is the preparation of alkali cellulose (soda cellulose) by treating cellulose with concentrated sodium hydroxide. Ethyl cellulose is made by reacting alkali cellulose with ethyl chloride.



Ethyl cellulose is produced in pellet form for molding and extrusion and in sheet form for fabrication. It has good processability, is tough, and is moderately flexible; its outstanding feature is its toughness at low temperatures. The principal uses of ethyl cellulose moldings are thus in those applications where good impact strength at low temperatures is required, such as refrigerator bases and flip lids and ice-crusher parts. Ethyl cellulose is often employed in the form of hot melt for strippable coatings used for protection of metal parts against corrosion and maring during shipment and storage. A recent development is the use of ethyl cellulose gel lacquers for permanent coatings.

Methyl cellulose is prepared by reacting alkali cellulose with methyl chloride at 50–100°C (cf. Ethyl cellulose). With a degree of substitution of 1.6–1.8, the resultant either is soluble in cold water but not in hot water. It is used as a thickening agent and emulsifier in cosmetics, pharmaceuticals, ceramics, as a paper size, and in leather-tanning operations. Hydroxyethyl cellulose, produced by reacting alkali cellulose with ethylene oxide, is employed for similar purposes.

Reaction of alkali cellulose with sodium salt of chloroacetic acid yields sodium carboxymethyl cellulose (SCMC),



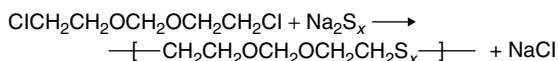
where $R = C_6H_7O_2$ and $m = 0.65-1.4$. SMC appears to be physiologically inert and is very widely used. Its principal application is as a soil-suspending agent in synthetic detergents, but it is also used as a sizing and finishing agent for textile, as a surface active agent, and as a viscosity modifier in emulsion and suspension. Purified grades of SMC are used in ice cream to provide a smooth texture and in a number of cosmetic and pharmaceutical products. SMC is also the basis of a well-known proprietary wallpaper adhesive.

4.3.7 Sulfide Polymers

4.3.7.1 Polysulfides

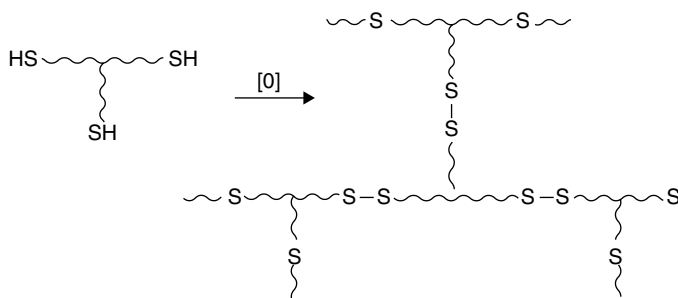
Monomers	Polymerization	Major Uses
Aliphatic dihalide, sodium sulfide	Polycondensation	Sealing, caulks, gaskets

Polysulfide elastomers are produced by the reaction of an aliphatic dihalide, usually bis(2-chloroethyl)formal, with sodium polysulfide under alkaline conditions:



The reaction is carried out with the dihalide suspended in an aqueous magnesium hydroxide phase. The value of x is slightly above 2. A typical polymerization system also includes up to 2% 1,2,3-trichloropropane. The polymerization occurs readily yielding a polymer with a very high molecular weight.

High molecular weight, however, is not desirable until its end-use application. The molecular weight is therefore lowered, and the *polysulfide rank* (value of x) is simultaneously brought close to 2, by reductive treatment with $NaSH$ and Na_2SO_3 followed by acidification. The result is a liquid, branched polysulfide with terminal thiol end group and a molecular weight in the range of 1000–8000. Curing to a solid elastomer is accomplished by oxidation of thiol to disulfide links by oxidants such as lead dioxide and *p*-quinone dioxime:



These materials are widely used as sealants, binders for solid propellants, caulking materials, and cements for insulating glass and fuel tanks.

Polysulfides, often referred to as *thiokols*, are produced at low volumes as specialty materials geared toward a narrow market. The advantages and disadvantages of polysulfides both reside in the disulfide linkage. Thus they possess low-temperature flexibility and very good resistance to ozone, oil, solvent (hydrocarbons as well as polar solvents such as alcohols, ketones, esters, etc.), and weathering. However, polysulfides have poor thermal stability and creep resistance, have low resilience, and are malodorous.

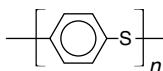
Thiokols are amorphous polymers which do not crystallize when stretched and hence reinforcing fillers, such as carbon black, must be added to obtain relatively high tensile strengths. Thiokol may be

vulcanized in the presence of zinc oxide and thiuram accelerators, such as tetramethyl-thiuram disulfide (*Tuads*). The accelerators modify the sulfur links and serve as chemical plasticizers.

A typical thiokol with 60 parts carbon black per 100 of polymer has a tensile strength of 1200 lbf/in.², an elongation of 300%, a specific gravity of 1.25, and a Shore A hardness of 68. Thiokol has excellent resistance to ozone (O₃) and ultraviolet radiation. It has a low permeability to solvents, such as gasoline; esters, such as ethyl acetate; and ketones, such as acetone.

The principal application of solid Thiokol elastomers is as gaskets, O-rings, gasoline, and fuel hose lines, gas meter diaphragms, and as rollers, which are used for lacquering cans.

4.3.7.2 Poly(Phenylene Sulfide)



Monomers	Polymerization	Major Uses
<i>p</i> -Dichlorobenzene, sodium sulfide	Polycondensation	Electrical components, mechanical parts

Poly(phenylene sulfide) (PPS) is the thio analogue of poly(phenylene oxide) (PPO) [57]. The first commercial grades were introduced by Phillips Petroleum in 1968 under the trade name Ryton. Other manufacturers also have introduced PPS (e.g., Tedur by Bayer). The commercial process involves the reaction of *p*-dichlorobenzene with sodium sulfide in a polar solvent.

PPS is an engineering plastic. The thermoplastic grades of PPS are outstanding in heat resistance, flame resistance, chemical resistance, and electrical insulation characteristics. The linear polymers are highly crystalline with melting point in the range of 285–295°C and *T_g* of 193–204°C.

The material is soluble only above 200°C in aromatic and chlorinated aromatic solvents. It has the ability to cross-link by air-oxidation at elevated temperatures, thereby providing an irreversible cure. Thermogravimetric analysis shows no weight loss below 500°C in air but demonstrates complete decomposition by 700°C. It is found to retain its properties after four months at 233°C (450°F) in air.

Significant increases in mechanical properties can be achieved with glass-fiber reinforcement. In the unfilled form the tensile strength of the material is 64–77 MPa at 21°C, 33 MPa at 204°C, and the flexural modulus is 4200 MPa at 21°C. The corresponding values for PPS–glass fiber (60:40) composites are 150, 33, and 15,500 MPa.

Although rigidity and tensile strength are similar to those of other engineering plastics, PPS does not possess the toughness of amorphous materials, such as the polycarbonates and the polysulfones (described later), and are somewhat brittle. On the other hand, PPS does show a high level of resistance to environmental stress cracking.

Being one of the most expensive commercial moldable thermoplastics, the use of PPS is heavily dependent on its particular combination of properties. Good electrical insulation characteristics, including good arcing and arc-tracking resistance have led to PPS replacing some of the older thermosets in electrical parts. These include connectors, terminal blocks, relay components, brush holders, and switch components.

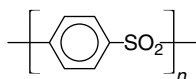
PPS is used in chemical process plants for gear pumps. It has found application in the automotive sector, in such specific uses as carburetor parts, ignition plates, flow control valves for heating systems, and exhaust-gas return valves to control pollution. The material also finds uses in sterilizable medical, dental, and general laboratory equipment, cooking appliance, and hair dryer components.

Injection-molded products of PPS include high-temperature lamp holders and reflectors, pump parts, valve, and, especially when filled for example with PTFE or graphite, bearings. Processing temperatures are 300–350°C with mold temperatures of up to 200°C. PPS is also used for encapsulation of electronic components and as a high temperature surface coating material.

PPS is resistant to neutron and gamma radiation. In nuclear installations, its flexural strength and modulus are essentially unchanged when it is exposed to gamma radiation of 5×10^9 rad and neutron radiation of 1×10^9 rad.

4.3.8 Polysulfones

Polysulfones are a family of engineering thermoplastics with excellent high-temperature properties. The simplest aromatic polysulfone, poly(*p*-phenylene sulfone)



does not show thermoplastic behavior, melting with decomposition above 500°C. Hence, to obtain a material capable of injection molding in conventional machines, the polymer chain is made more flexible by incorporating ether links into the backbone.

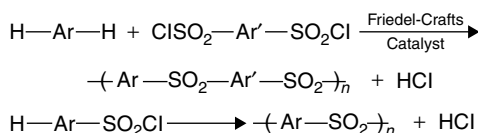
The structures and glass transition temperatures of several commercial polysulfones are listed in Table 4.30. The polymers have different degrees of spacing between the *p*-phenylene groups and thus have a spectrum of glass transition temperatures which determine the heat-distortion temperature (or deflection temperature under load), since the materials are all amorphous.

The first commercial polysulfone (Table 4.30I) was introduced in 1965 by Union Carbide. This material, now known as Udel, has a continuous-use temperature of 150°C and a maximum-use temperature of 170°C, and it can be fabricated easily by injection molding in conventional machines.

In 1967, Minnesota Mining and Manufacturing (3M) introduced Astrel 360 (Table 4.30II), an especially high-performance thermoplastic, which requires specialized equipment with extra heating and pressure capabilities for processing. ICI's polyether sulfones, introduced in 1972—Victrex (Table 4.30III) and polyethersulfone 720P (Table 4.30IV)—are intermediate in performance and processing. In the late 1970s, Union Carbide introduced Radel (Table 4.30V), which has a higher level of toughness. Note that all of the commercial materials mentioned in Table 4.30 may be described as polysulfones, polyarylsulfones, polyether sulfones, or polyaryl ether sulfones.

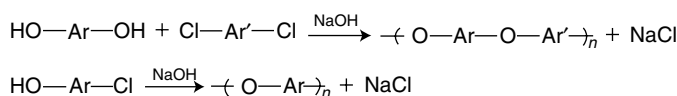
In principle, there are two main routes to the preparation of polysulfones: (1) polysulfonylation and (2) polyetherification.

Polysulfonylation reactions are of the following general types:



The Ar and/or Ar' group(s) contain an ether oxygen, and if Ar=Ar', then basically identical products may be obtained by the two routes.

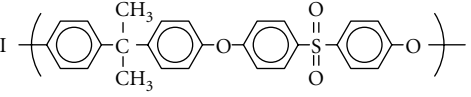
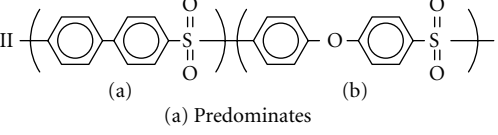
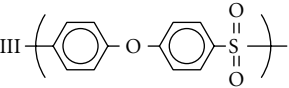
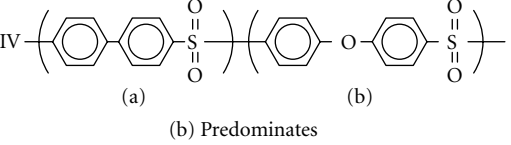
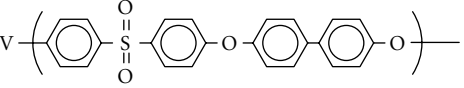
In the *polyetherification* route the condensation reaction proceeds by reactions of types

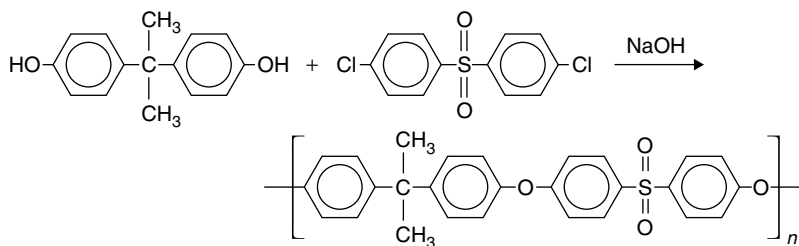


The Ar and/or Ar' group(s) contain sulfone groups, and if Ar=Ar', then identical products may be obtained by the two routes.

Polyetherification processes form the basis of commercial polysulfone production methods. For example, the Udel-type polymer (Union Carbide) is prepared by reacting, 4,4'-dichlorodiphenylsulfone with an alkali salt of bisphenol A. The polycondensation is conducted in highly polar solvents, such as dimethylsulfoxide or sulfolane.

TABLE 4.30 Commercial Polysulfones

Type of Structure	T_g (°C)	Trade Name
I 	190	Udel (Union Carbide)
II  (a) Predominates	285	Astrel (3M Corp.)
III 	230	Victrex (ICI)
IV  (b) Predominates	250	Polyether-Sulfone 720 P (ICI)
V 	—	Rodel (Union Carbide)



4.3.8.1 Properties

In spite of their linear and regular structure the commercial polysulfones are amorphous. This property might be attributed to the high degree of chain stiffness of polymer molecules which make crystallization difficult. Because of their high in-chain aromaticity and consequent high chain stiffness, the polymers have high values of T_g (see Table 4.30), which means that the processing temperatures must be above 300°C.

Commercial polymers generally resist aqueous acids and alkalis but are attacked by concentrated sulfuric acid. Being highly polar, the polymer is not dissolved by aliphatic hydrocarbons but dissolves in dimethyl formamide and dimethyl acetamide.

In addition to the high heat-deformation resistance, the polymers also exhibit a high degree of chemical stability. This has been ascribed to an enhanced bond strength arising from the high degree of resonance in the structure. The polymers are thus capable of absorbing a high degree of thermal and ionizing radiation without cross-linking.

The principal features of commercial polysulfones are their rigidity, transparency, self-extinguishing characteristics, exceptional resistance to creep, especially at somewhat elevated temperatures, and good high-temperature resistance.

The use temperatures of the major engineering thermoplastics are compared in Figure 4.36. Polysulfones are among the higher-priced engineering thermoplastics and so are only considered when polycarbonates or other cheaper polymers are unsuitable. In brief, polysulfones are more heat resistant and have greater resistance to creep, whereas polycarbonates have a somewhat higher Izod and tensile impact strength besides being less expensive.

In many fields of use polysulfones have replaced or are replacing metals, ceramics, and thermosetting plastics, rather than other thermoplastics. Since commercial polysulfones can be injection molded into complex shapes, they avoid costly machining and finishing operations. Polysulfones can also be extruded into film and foil. The latter is of interest for flexible printed circuitry because of its high-temperature performance.

Polysulfones have found widespread use where good dimensional stability at elevated temperatures is required and fabrication is done by injection molding. Some products made from polysulfones are electrical components, connectors, coil bobbins, relays, and appliances operating at high temperatures (e.g., hair driers, fan heaters, microwave ovens, lamp housings and bases).

Polysulfones are transparent (though often slightly yellow), have low flammability (limiting oxygen index typically 38), and burn with little smoke production. Typical properties of some of the commercial polysulfones are shown in Table 4.31.

4.3.9 Polyether Ketones

The chemistry and technology of aromatic polyether ketones may be considered as an extension to those of the polysulfones [58]. The two polymer classes have strong structural similarities, and there are strong parallels in preparative methods.

Preparations reported for aromatic polyether ketones are analogous to the polysulfonylation and polyetherification reactions for the polysulfones. Several aromatic polyether ketones have been prepared.

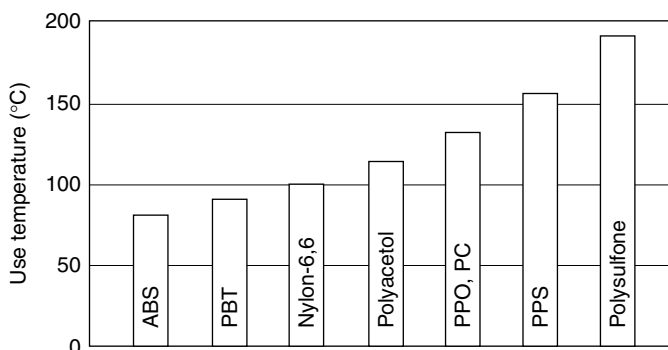
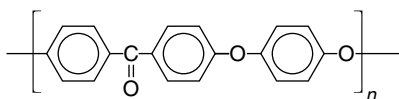


FIGURE 4.36 Use temperatures of major engineering thermoplastics.

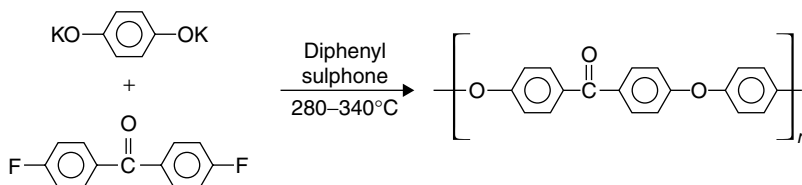
TABLE 4.31 Properties of Aromatic Polysulfones

Property	Udel (Union Carbide)	Victrex (ICI)	Astrel (3M)
Tensile strength			
10 ³ lbf/in. ²	9.3	12.2	13.0
MPa	64	84	90
Tensile modulus			
10 ⁵ lbf/in. ²	3.6	3.5	3.8
GPa	2.5	2.4	2.6
Elongation at break (%)	50–100	40–80	10
Flexural modulus			
10 ⁵ lbf/in. ²	3.0	3.8	4.0
GPa	2.1	2.6	2.8
Heat distortion temperature (°C)	174	203	274
Impact strength, notched Izod	—	1.9	—
ft.-lb/in.			
J/m	—	100	—
Limiting oxygen index (%)	—	38	—

The polyether ether ketone (PEEK) was test marketed in 1978 by ICI.



PEEK is made by the reaction of the potassium salt of hydroquinone with difluorobenzophenone in a high boiling solvent, diphenylsulfone, at temperatures close to the melting point of the polymer:



PEEK is semicrystalline with a melting temperature (T_m) of 335°C and a glass transition temperature (T_g) of 145°C. The degree of crystallinity can vary from 40% (slow cooling) to essentially amorphous (quenching), but is usually about 35%.

PEEK is a high-temperature-resistant thermoplastic suitable for wire coating, injection molding, film and advanced structural composite fabrication. The wholly aromatic structure of PEEK contributes to its high-temperature performance.

The polymer exhibits very low water absorption, very good resistance to water at 125°C (under which conditions other heat-resisting materials, such as aromatic polyamides, are liable to fail), and is resistant to attack over a wide pH range, from 60% sulfuric acid to 40% sodium hydroxide at elevated temperatures, although attack can occur with some concentrated acids.

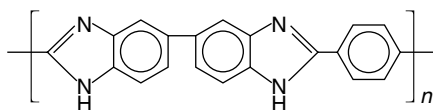
PEEK has outstanding resistance to both abrasion and dynamic fatigue. Its tensile strength decreases less than 10% after 10⁷ cycles at 23°C. It has low flammability with a limiting oxygen index of 35% and generates an exceptionally low level of smoke. Other specific features are excellent resistance to gamma radiation and good resistance to environmental stress cracking.

PEEK has greater heat resistance compared to poly(phenylene sulfide) and is also markedly tougher (and markedly more expensive). PEEK is melt processable and may be injection molded and extruded on conventional equipment.

Typical applications of PEEK include coating and insulation for high-performance wiring, particularly for the aerospace and computer industries, military equipment, nuclear plant applications, oil wells, and compressor parts.

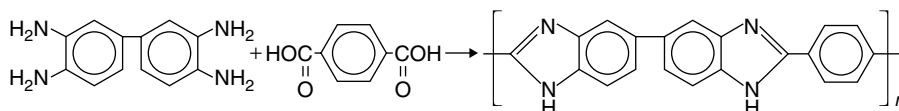
Since it is a crystalline polymer, the strength and thermal resistance of PEEK are increased dramatically by incorporation of reinforcing agents. Composite prepegs with carbon fibers have been developed for structural aircraft components. Typical properties of PEEK are shown in Table 4.32.

4.3.10 Polybenzimidazole



Monomers	Polymerization	Major Uses
Tetraaminobiphenyl, terephthalic acid	Polycondensation	Fiber

Polybenzimidazole (PBI) is the most well-known commercial example of aromatic heterocycles used as high-temperature polymers. The synthesis of PBI is carried out as follows (see also Figure 1.36). The tetraaminobiphenyl required for the synthesis of PBI is obtained from 3,3'-dichloro-4,4'-diaminodiphenyl (a dye intermediate) and ammonia. Many other tetraamines and dicarboxylic acids have been condensed to PBI polymeric systems.



The high thermal stability of PBI (use temperature about 400°C compared to about 300°C for polyimides) combined with good stability makes it an outstanding candidate for high-temperature application despite its relatively high cost.

Fibers have been wet spun from dimethylacetamide solution, and a deep gold woven cloth has been made from this fiber by Celanese. The cloth is said to be more comfortable than cotton (due to high moisture retention) and has greater flame resistance than Nomex (oxygen index of 29% for PBI compared to 17% for Nomex). The U.S. Air Force has tested flight suits of PBI and found them superior to other materials.

TABLE 4.32 Properties of Polyetheretherketone

Property	Unfilled	30% Glass Fiber Filled
Tensile strength		
10 ³ lbf/in. ²	13.3	22.8
MPa	92	157
Elongation at break (%)	4.9 (yield)	2.2
Flexural modulus		
10 ⁵ lbf/in. ²	5.4	14.9
GPa	3.7	10.3
Impact strength, notched Izod		
ft.-lb/in.	1.6	1.8
J/m	83	96
Heat distortion temperature (°C)	140	315
Limiting oxygen index (%)	35	—

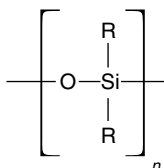
Other applications of PBI are in drogue parachutes and lines for military aircraft as well as ablative heat shields. The PBI fibers have also shown promise as reverse osmosis membranes and in graphitization to high-strength, high-modulus fibers for use in composites. The development of ultra-fine PBI fibers for use in battery separator and fuel cell applications has been undertaken by Celanese.

A new technique of simple precipitation has been used to process PBI polymers into films. High-strength molecular-composite films have been produced with tensile strength in the region of 20,000 psi (137 MPa). The PBI polymer has also been fabricated as a foam. The material provides a low-weight, high-strength, thermally stable, machinable insulation, much needed in the aerospace industry. PBIs exhibit good adhesion as films when cast from solution onto glass plates. This property leads to their use in glass composites, laminates, and filament-wound structures.

4.3.11 Silicones and Other Inorganic Polymers

The well-known thermal stability of minerals and glasses, many of which are themselves polymeric, has led to intensive research into synthetic inorganic and semi-inorganic polymers [14,59,60]. Numerous such polymers have been synthesized, but only a few have found industrial acceptance, due to the difficulties encountered in processing them.

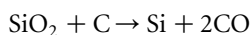
4.3.11.1 Silicones



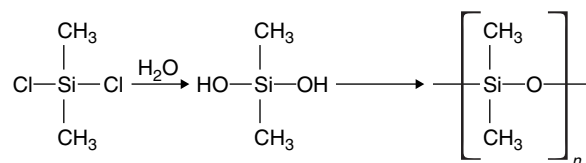
Monomer	Polymerization	Major Uses
Chlorosilanes	Polycondensation	Elastomer, sealants, and fluids

Silicones are by far the most important inorganic polymers and are based on silicon, an element abundantly available on our planet. The silicone polymers are available in a number of forms, such as fluids, greases, rubbers, and resins. Because of their general thermal stability, water repellency, antiadhesive characteristics, and constancy of properties over a wide temperature range, silicones have found many and diverse applications. [The structure used as the basis of the nomenclature of the silicon compounds is silane SiH_4 , corresponding to methane CH_4 . Alkyl-, aryl-, alkoxy-, and halogen-substituted silanes are referred to by prefixing silane by the specific group present. For example, $(\text{CH}_3)_2\text{SiH}_2$ is dimethyl silane, and CH_3SiCl_3 is trichloromethylsilane. Polymers in which the main chain consists of repeating $-\text{Si}-\text{O}-$ units together with predominantly organic side groups are referred to as *polyorganosiloxanes* or, more loosely, as *silicones*.]

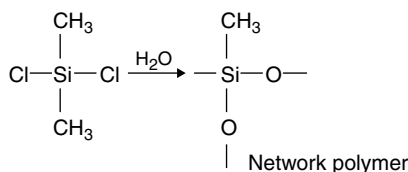
The commercial production of a broad variety of products from a few basic monomers followed the development of an economically attractive direct process for chlorosilanes, discovered by E. G. Rochow in 1945 at the G. E. Research Laboratories. The process involves reaction of alkyl or aryl halides with elementary silicon in the presence of a catalyst, e.g., copper for methyl- and silver for phenylchlorosilanes. The basic chemistry can be described as



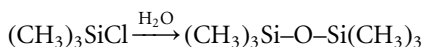
In the alkylation of silicon with methyl chloride, mono-, di-, and trimethyl chlorosilanes are formed. The reaction products must then be fractionated. Because the dimethyl derivative is bifunctional, it produces linear methylsilicone polymers on hydrolysis.



Since monomethyl trichlorosilane has a functionality of 3, the hydrolysis leads to the formation of a highly cross-linked gel.



Since the trimethyl monochlorosilane is monofunctional, it forms only a disiloxane.



Products of different molecular-weight ranges and degrees of cross-linking are obtained from mixtures of three chlorosilanes in different ratios. In characterizing commercial branched and network structures, the CH_3/Si ratio (or, generally, R/Si ratio) is thus a useful parameter. For example, the preceding three idealized products have CH_3/Si ratios of 2:1, 1:1, and 3:1, respectively. A product with a CH_3/Si ratio of 1.5:1 will thus be expected to have a moderate degree of cross-linking.

Many different silicon products are available today. The major applications are listed in [Table 4.33](#).

4.3.11.1.1 Silicone Fluids

The silicone fluids form a range of colorless liquids with viscosities from 1 to 1,000,000 centistokes (cs). The conversion of chlorosilane intermediates into polymer is accomplished by hydrolysis with water, which is followed by spontaneous condensation. In practice, the process involves three important stages: (1) hydrolysis, condensation, and neutralization (of the HCl evolved on hydrolysis); (2) catalytic equilibration; and (3) devolatilization.

The product after the first stage consists of an approximately equal mixture of cyclic compounds, mainly the tetramer, and linear polymer. To achieve a more linear polymer and also to stabilize the viscosity, it is common practice to equilibrate the products of hydrolysis by heating with a catalyst such as dilute sulfuric acid. For fluids of viscosities below 1000 cs, this equilibrium reaction is carried out for hours at 100–150°C.

After addition of water, the oil is separated from the aqueous acid layer and neutralized. To produce nonvolatile silicone fluids, volatile low-molecular products are removed by using a vacuum still. Commercial nonvolatile fluids have a weight loss of less than 0.5% after 24 h at 150°C.

Dimethylsilicone fluids find a wide variety of applications mainly because of their water repellency, lubrication and antistick properties, low surface tension, a high order of thermal stability, and a fair constancy of physical properties over a wide range of temperature (–70°C to 200°C).

As a class the silicone fluids have no color or odor, have low volatility, and are nontoxic. The fluids have reasonable chemical resistance but are attacked by concentrated mineral acids and alkalis. They are soluble in aliphatic, aromatic, and chlorinated hydrocarbons.

A well-known application of the dimethylsilicone fluids is as a polish additive. The value of the silicone fluids in this application is due to its ability to lubricate, without softening, the microcrystalline wax plates.

Dilute solutions or emulsions containing 0.5–1% of a silicone fluid are extensively used as a release agent for rubber molding. However, their use has been restricted with thermoplastics because of the tendency of the fluids to cause stress cracking in polymers.

Silicone fluids are used in shock absorbers, hydraulic fluids, dashpots, and in other damping systems in high-temperature operations.

TABLE 4.33 Major Applications of Silicones

Mold-release agents	Greases and waxes
Water repellants	Cosmetics
Antifoaming agents	Insulation
Glass-sizing agents	Dielectric encapsulation
Heat-exchange fluids	Caulking agents (RTV)
Hydraulic fluids	Gaskets and seals
Surfactants	Laminates
Coupling agents	Biomedical devices

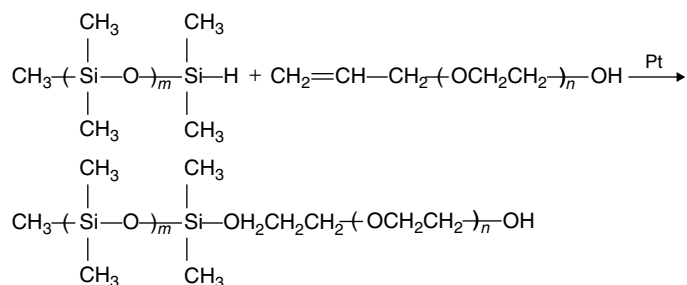
The silicones have established their value as water-repellent finishes for a range of natural and synthetic textiles. Techniques have been developed which result in the pickup of 1–3% of silicone on the cloth. Leather also may be made water repellent by treatment with solutions or emulsions of silicone fluids. These solutions are also used for paper treatment.

Silicone fluids and greases are useful as lubricants for high-temperature operations for applications depending on rolling friction. Grease may be made by blending silicone with an inert filler such as fine silicas, carbon black, or a metallic soap. The silicone/silica greases are used as electrical greases for such applications as aircraft and car ignition systems. Silicone greases have also found uses in the laboratory for lubricating stopcocks and for high-vacuum work.

Silicone fluids are used extensively as antifoams, although concentration needed is normally only a few parts per million. The fluids have also found a number of uses in medicine. Barrier creams based on silicone fluids are particularly useful against cutting oils used in metal machinery processes.

High-molecular-weight dimethylsilicone fluids are used as stationary phase for columns in vapor-phase chromatographic apparatus.

Surfactants based on block copolymers of dimethylsilicone and poly(ethylene oxide) are unique in regulating the cell size in polyurethane foams. One route to such polymers used the reaction between a polysiloxane and an allyl ether of poly(ethylene oxide),



where $m=2-5$ and $n=3-20$. Increasing the silicone content makes the surfactant more lipophilic, whereas a higher poly(ethylene oxide) content makes it more hydrophilic.

4.3.11.1.2 Silicone Resins

Silicone resins are manufactured batchwise by hydrolysis of a blend of chlorosilanes. For the final product to be cross-linked, a certain amount of trichlorosilane must be incorporated into the blend. (In commercial practice, R/Si ratios are typically in the range of 1.2:1–1.6:1) The cross-linking of the resin is, of course, not carried out until it is in situ in the finished product. The cross-linking takes place by heating the resin at elevated temperatures with a catalyst, several of which are described in the literature (e.g., triethanolamine and metal octoates).

The resins have good heat resistance but are mechanically much weaker than cross-linked organic plastics. The resins are highly water repellent and are good electrical insulators particularly at elevated temperatures and under damp conditions. The properties are reasonably constant over a fair range of temperature and frequency.

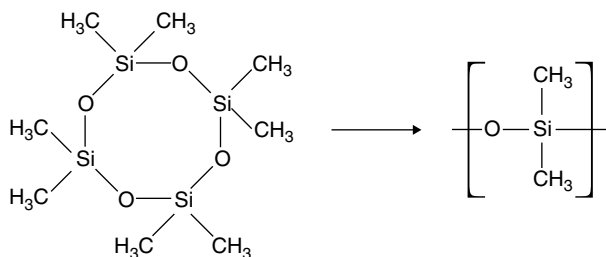
Methyl phenyl silicone resins are used in the manufacture of heat-resistant glass-cloth laminates particularly for electrical applications. These are generally superior to PF and MF glass-cloth laminates. The dielectric strength of silicon-bonded glass-cloth laminates is 100–120 kV/cm compared to 60–80 kV/cm for both PF and MF laminates. The insulation resistance (dry) of the former (500,000 Ω) is significantly greater than those for the PF and MF laminates (10,000 and 20,000 Ω , respectively). The corresponding values after water immersion are 10,000, 10, and 10 Ω .

Silicone laminates are used principally in electrical applications such as printed circuit boards, transformers, and slot wedges in electric motors, particularly class H motors. Compression-molding powders based on silicone resins are available and have been used in the molding of switch parts, brush ring holders, and other electrical applications that need to withstand high temperatures.

4.3.11.1.3 Silicone Rubbers

Silicone elastomers are either *room-temperature vulcanization* (RTV) or *heat-cured silicone rubbers*, depending on whether cross-linking is accomplished at ambient or elevated temperature. [The term *vulcanization* (see [Chapter 1](#) and [Chapter 2](#)) is a synonym for cross-linking. While *curing* is also a synonym for cross-linking, it often refers to a combination of additional polymerization plus cross-linking.] RTV and heat-cured silicone rubbers typically involve polysiloxanes with degrees of polymerizations of 200–1500 and 2500–11,000, respectively.

While the lower-molecular-weight polysiloxanes can be synthesized by the hydrolytic step polymerization process, the higher-molecular-weight polymers are synthesized by ring-opening polymerization using ionic initiators:



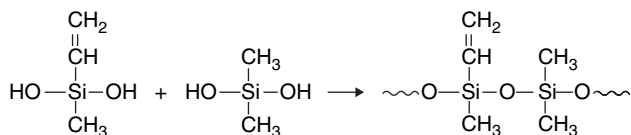
The cyclic tetramer (octamethylcyclotetrasiloxane) is equilibrated with a trace of alkaline catalyst for several hours at 150–200°C, the molecular weight being controlled by careful addition of monofunctional siloxane. The product is a viscous gum with no elastic properties.

Before fabrication it is necessary to compound the gum with fillers, a curing agent, and other special additives on a two-roll mill or in an internal mixer (see Rubber Compounding, [Chapter 2](#)). Unfilled polymers have negligible strength, whereas reinforced silicone rubbers may have strengths up to 2000 psi (14 MPa).

Silica fillers are generally used with silicone rubbers. These materials with particle sizes in the range 0.003–0.03 μm are prepared by combustion of silicon tetrachloride (fume silicas), by precipitation, or as an aerogel.

Heat-curing of silicone rubbers usually involve free-radical initiators such as benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, and *t*-butyl per-benzoate, used in quantities of 0.5–3%. These materials are stable in the compounds at room temperature for several months but will start to cure at about 70°C. The curing (cross-linking) is believed to take place by the sequence of reactions shown in [Figure 4.37](#). The process involves the formation of polymer radicals via hydrogen abstraction by the peroxy radicals formed from the thermal decomposition of the peroxide and subsequent cross-linking by coupling of the polymer radicals.

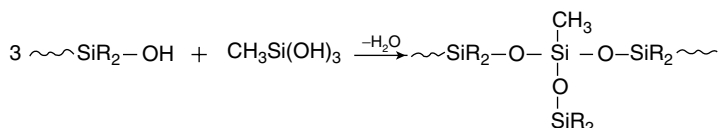
The cross-linking efficiency of the peroxide process can be increased by incorporating small amounts of a comonomer containing vinyl groups into the polymer, e.g., by copolymerization with small amounts of vinyl-methyl silanol:



Dimethyl silicone rubbers show a high compression set. (For example, normal cured compounds have a compression set of 20–50% after 24 h at 150°C.) Substantially reduced compression set values may be obtained by using a polymer containing small amounts of methylvinylsiloxane. Rubbers containing vinyl groups can be cross-linked by weaker peroxide catalysts. Where there is a high vinyl content (4–5% molar), it is also possible to vulcanize with sulfur.

Room-temperature vulcanizing silicone rubbers (RTV rubbers) are low-molecular-weight liquid silicones with reactive end groups and loaded with reinforcing fillers. Several types are available on the market.

“One-component” RTV rubbers consist of an air-tight package containing silanol-terminated polysiloxane, cross-linking agent (methylacetoxysilane), and catalyst (e.g., dibutyltin laurate). Moisture from the atmosphere converts the cross-linking agent to the corresponding silanol (acetic acid is a by-product), $\text{CH}_3\text{Si}(\text{OH})_3$, which brings about further polymerization combined with cross-linking of the polysiloxane,



Two-component RTV formulations involve separate packages for the polysiloxane and cross-linking agent. A typical two-component RTV formulation cures by reaction of silanol end groups with silicate esters in the presence of a catalyst such as tin octoate or dibutyltin dilaurate (Figure 4.38).

Another two-pack RTV formulation cures by hydrosilation, which involves the addition reaction between a polysiloxane containing vinyl groups (obtained by including methylvinylchlorosilane in the original reaction mixture for synthesis of polysiloxane) and a siloxane cross-linking agent that contains Si–H functional groups, such as $\text{Si}[\text{OSi}(\text{CH}_3)_2\text{H}]_4$. The reaction is catalyzed by chloroplatinic acid or other soluble platinum compounds.

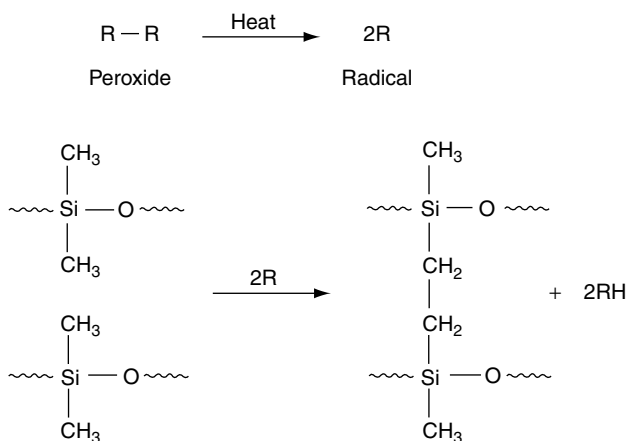
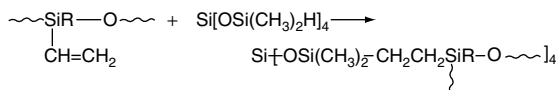


FIGURE 4.37 Peroxide curing of silicone rubbers.



Hydride functional siloxanes can also cross-link silanol-terminated polysiloxanes. The reaction is catalyzed by tin salts and involves elimination of H_2 between Si-H and Si-O-H groups.

RTV rubbers have proved to be of considerable value as they provide a method for producing rubbery products with the simplest equipment. These rubbers find use in the building industry for caulking and in the electrical industry for encapsulation.

Nontacky self-adhesive rubbers (fusible rubbers) are obtained if small amounts of boron (~ 1 boron atom per 300 silicon atoms) are incorporated into the polymer chain. They may be obtained by condensing dialkylpolysiloxanes end-blocked with silanol groups with boric acid or by reacting ethoxyl end-blocked polymers with boron triacetate.

Bouncing putty is somewhat similar in that the Si-O-B bond occurs occasionally along the chain. It is based on a polydimethylsiloxane polymer modified with boric acid, additives, fillers, and plasticizers to give a material that shows a high elastic rebound when small pieces are dropped on a hard surface but flows like a viscous fluid on storage or slow application of pressure.

The applications of the rubbers stem from their important properties, which include thermal stability, good electrical insulation properties, nonstick properties, physiological inertness, and retention of elasticity at low temperatures. The temperature range of general-purpose material is approximately -50°C to $+250^\circ\text{C}$, and the range may be extended with special rubbers. Silicone rubbers are, however, used only as special-purpose materials because of their high cost and inferior mechanical properties at room temperature as compared to conventional rubbers (e.g., natural rubber and SBR).

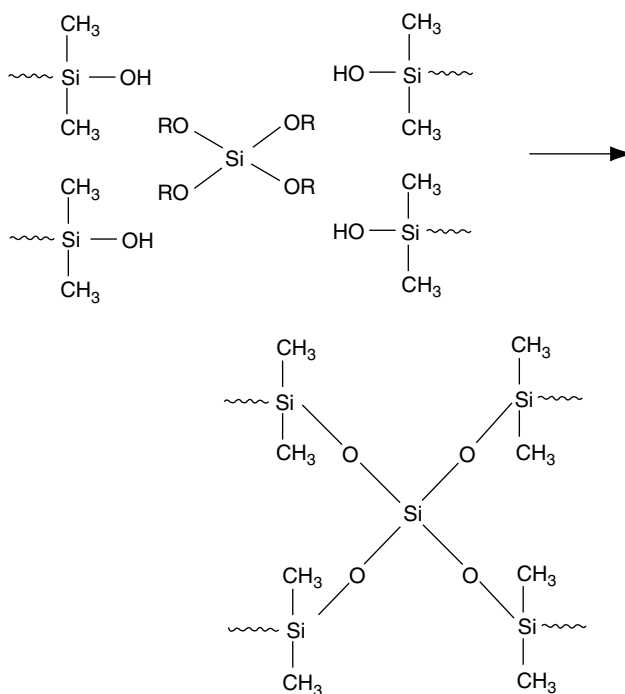


FIGURE 4.38 Curing of RTV rubbers by reaction of silanol end groups with silicate esters in the presence of a catalyst such as tin octoate or dibutyltin dilaurate.

Modern passenger and military aircraft each use about 500 kg of silicone rubber. This is to be found in gaskets and sealing rings for jet engines, vibration dampers, ducting, sealing strips, and electrical insulators. Silicone cable insulation is also used extensively in naval craft since the insulation is not destroyed in the event of fire but forms an insulating layer of silica.

The rubbers find use in diverse other applications which include electric iron gaskets, domestic refrigerators, antibiotic container closures, and for nonadhesive rubber-covered rollers for handling such materials as confectionary and adhesive tape.

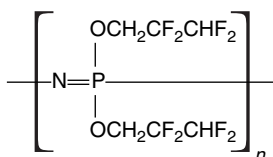
Due to their relative inertness, new applications have emerged in the biomedical field. A silicone rubber ball is used in combination with a fluorocarbon seal to replace defective human heart valves. Silicone rubber has had many applications in reconstructive surgery on or near the surface of the body. Prosthetic devices are very successfully used in all parts of the body.

The cold-curing silicone rubbers are of value in potting and encapsulation.

Liquid silicone rubbers may be considered as a development from the RTV silicone rubbers but they have a better pot life and improved physical properties, including heat stability (in the cured state) similar to that of conventional silicone elastomers. Liquid silicone rubbers range from a flow consistency to a paste consistency and are usually supplied as a two-pack system, which requires simple blending before use. The materials cure rapidly above 110°C. In injection molding of small parts at high temperatures (200–250°C), cure times may be as small as a few seconds. One example of application is in baby bottle nipples, which, although more expensive, have a much longer working life.

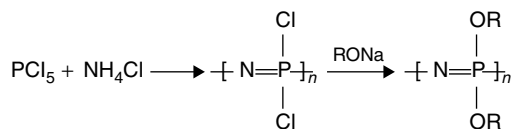
Liquid silicone rubbers have also been used in some extruded applications. Vulcanization of the extruded material may be carried out by using infrared heaters or circulated hot air. The process has been applied to wire coating, ignition cables, optical fibers, various tapes, and braided glass-fiber sleeving, as well as for covering delicate products.

4.3.11.2 Polyphosphazenes



Monomers	Polymerization	Major Uses
Phosphorus pentachloride, ammonium chloride, fluorinated alcohols	Polycondensation followed by nucleophilic replacement of chloro-groups	Aerospace, military, oil exploration applications

Polyphosphazenes containing nitrogen and phosphorus have been synthesized by replacing the chlorine atoms on the backbone chain of polymeric phosphonitrilic chloride (dichlorophosphazene) by alkoxy or fluoroalkoxy groups. These derivative polymers do not exhibit the hydrolytic instability of the parent polymer. The general synthesis scheme is



With mixtures of alkoxy substituents having longer alkyl chains, crystallization can be avoided to produce an amorphous rubber. The product is referred to as phosphonitrilic fluoroelastomer, a semiorganic rubber. The rubber can be cross-linked with free-radical initiators or by radiation. A

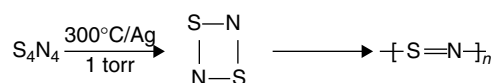
commercial rubber (PNF by Firestone Tire and Rubber Co.) is based on alkoxides of trifluoroethyl alcohol or heptafluoroisobutyl alcohol.

The polyphosphazene rubbers have excellent resistance to oils and chemicals (except alcohols and ketones), good dynamic properties, good abrasion resistance, and a broad range of use temperatures (-65°C to $+117^{\circ}\text{C}$). The water resistance, however, is only fairly good.

4.3.11.3 Polythiazyl

Monomer	Polymerization	Major Uses
S_4N_4	Ring-opening polymerization	Semiconductive polymers

The solid four-member ring reaction product S_2N_2 obtained by pyrolysis of gaseous S_4N_4 under vacuum is polymerized at room temperature by ring-opening polymerization to give the linear chain polythiazyl.



The product is a brasslike solid material that behaves like a metal or alloy but is lighter and more flexible. Polythiazyl has electrical conductivity (3700 reciprocal ohm-cm, or siemens/cm) at room temperature and super-conductivity at 0.3 K. Some doped polymers are photoconductive.

4.3.12 Polyblends

The concept of physically blending two or more existing polymers or copolymers to obtain new products or for problem solving is now attracting widespread interest and commercial utilization [61–65]. By definition, any physical mixture of two or more different polymers or copolymers that are not linked by covalent bonds is a *polymer blend* or *polyblend*.

Blends have been classified as miscible one-phase systems and partially miscible or immiscible two-phase systems. A negative change in free energy (ΔG) is required for miscibility. The change in entropy (ΔS) is essentially negligible, and hence the change in enthalpy (ΔH) must be negative or zero for the formation of miscible blends as shown by the Gibbs free energy equation:

$$\Delta G = \Delta H - T\Delta S$$

where T is the absolute temperature. The requirement for a negative ΔH value can be met when there is a physical attraction, such as hydrogen bonding, between the component polymers.

A polymer blend (PB) that is homogeneous down to the molecular level and is associated with the negative value of the free energy of mixing, $\Delta G = \Delta H \leq 0$, is termed a *miscible polymer blend*. An *immiscible polymer blend*, on the other hand, is any PB for which $\Delta G = \Delta H < 0$.

To make an analogy with metals polymer blends are sometimes referred to as *polymer alloys*. Thus the term alloy has been used to describe miscible or immiscible mixtures of polymers that are usually blended as melts. Another definition often used for a polymer alloy is that it is an immiscible PB having a modified interface and/or morphology. The general relationship between blends and alloys is shown in Figure 4.39. The term *compatibilization* in the figure refers to a process of modification of interfacial properties (discussed later) of an immiscible PB, leading to the creation of a polymer alloy.

The concept of blending polymers is not new; the rubber industry has used it for decades. In recent years, however, there has been a resurgence of interest arising primarily from the demand for engineering plastics and speciality polymers. There are sound economic reasons for this interest. Development of a new polymer to meet a specific need is a costly enterprise. If the desired properties can be realized simply by mixing two or more existing polymers, there is an obvious economic advantage. Since the time

normally required to develop a new blend is commercially 3–5 years, compared to 8–10 years required for new plastics materials. Moreover, the cost is reduced if an expensive polymer can be diluted by a less expensive one.

Blending provides a convenient way of combining the mechanical, physical, or thermal properties of more than one material. One example is the blend of ABS and PVC. The ABS contributes high heat-distortion temperature, toughness, and easy moldability, while the PVC imparts weatherability and flame retardance, as well as reducing the cost of the blend. Applications of the blend include automotive interior trim, luggage shells, and canoes.

Important disadvantages of a basic polymer (for example, difficulties of fabrication) may be overcome by blending with one or more other polymers. In some cases, synergistic improvement in properties, exceeding the value for either polymer alone, is achieved by blending, though such cases are relatively rare. A good example is the improved Izod notched impact strength shown when ABS and polycarbonate (PC) are blended. At subzero temperatures, the blend has better notched impact strength than either of its component polymers.

The first commercial blend of two dissimilar polymers was Noryl, a miscible polyblend of poly(phenylene oxide) and polystyrene, introduced by General Electric in the 1960s. Since that time a large number of different blends have been introduced. A number of technologies have been devised to prepare polyblends; these are summarized in Table 4.34. For economic reasons, however, mechanical blending predominates.

It so happens that most polymers are not miscible; rather they separate into discrete phases on being mixed. Differences between miscible and immiscible polyblends are manifested in appearance (miscible blends are usually clear, immiscible blends are opaque) and in such properties as glass transition temperature (miscible blends exhibit a single T_g intermediate between those of the individual components, whereas immiscible blends exhibit separate T_g s characteristic of each component).

Though miscibility is by no means a prerequisite to commercial utility, homogeneous polymer blends are more convenient from the standpoint of being able to predict properties or processing characteristics.

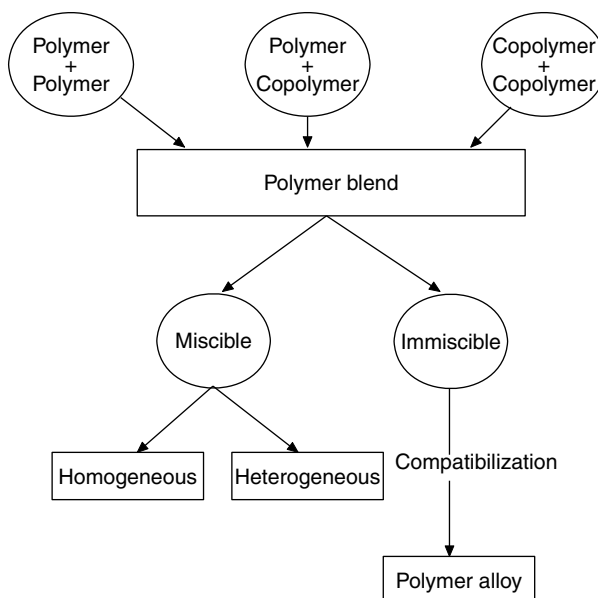


FIGURE 4.39 Schematic representation of the general relationship between polymer blends and alloys.

For example, if additives are used, there are no problems of migration from one phase to another. Physical or mechanical properties usually reflect, to a degree, the weighted average of the properties of each component. For a binary homogeneous blend, this can be expressed quantitatively for a particular property (P) by means of a semiempirical relationship:

$$P = \phi_1 P_1 + \phi_2 P_2 + \phi_1 \phi_2 I \quad (4.3)$$

where ϕ is the volume fraction in the mix and I is an interaction term that may be negative, zero, or positive. For $I=0$, the properties are strictly additive. If I is positive, the property in question is better than the weighted average and the blend is said to be *synergistic* for that property. However, if I is negative, the property is worse than the weighted average (*incompatible, nonsynergistic*). This is illustrated schematically in Figure 4.40 by a plot of property vs. composition.

In the case of complete miscibility, we would expect properties to follow a simple monotonic function, more or less proportional to the contents of the two polymer components in the blend (Figure 4.40a). This is particularly useful for processors because it permits them to inventory a few commodity polymers and simply blend them in different proportions to meet the specific requirements of each product they manufacture.

Noryl, for example, is composed of polystyrene, an inexpensive polymer, and poly(phenylene oxide) or PPO, a relatively expensive polyether. For the most, the properties of Noryl are additive. For example, Noryl has poorer thermal stability than the polyether alone, but is easier to process. Its single glass transition temperature increases with increasing polyether content. In terms of tensile strength, however, the polyblend is synergistic.

For two polymers to be completely miscible, the optimum requirements are similar polarity, low molecule weight, and hydrogen bonding or other strong intermolecular attraction. Most polymer pairs do not meet these requirements for complete theoretical miscibility. The free energy of mixing is positive, and they tend to separate into two phases.

If they are slightly immiscible, each phase will be a solid solution of minor polymer in major polymer, and the phases will separate into submicroscopic domains with the polymer present in major amount forming the continuous matrix phase and contributing most toward its properties. Plots of properties vs.

TABLE 4.34 Types and Methods of Producing of Polyblends

Type	Method of Blending
Mechanical blends	Polymers are mixed at temperatures above T_g or T_m for amorphous and semicrystalline polymers, respectively
Mechanochemical blends	Polymers are mixed at shear rates high enough to cause degradation. Resultant free radicals combine to form complex mixtures including block and graft components
Solution-cast blends	Polymers are dissolved in common solvent and solvent is removed
Latex blends	Fine dispersions of polymers in water (latexes) are mixed, and the mixed polymers are coagulated
Chemical blends	
Interpenetrating polymer networks (IPN)	Cross-linked polymer is swollen with a different monomer; the monomer is then polymerized and cross-linked
Semi-interpenetrating polymer networks (semi-IPN, also called pseudo-IPN)	Polyfunctional monomer is mixed with thermoplastic polymer, then monomer is polymerized to network polymer
Simultaneous interpenetrating polymer networks (SIN)	Different monomers are mixed, then homopolymerized and cross-linked simultaneously
Interpenetrating elastomeric networks (IEN)	Latex polyblend is cross-linked after coagulation

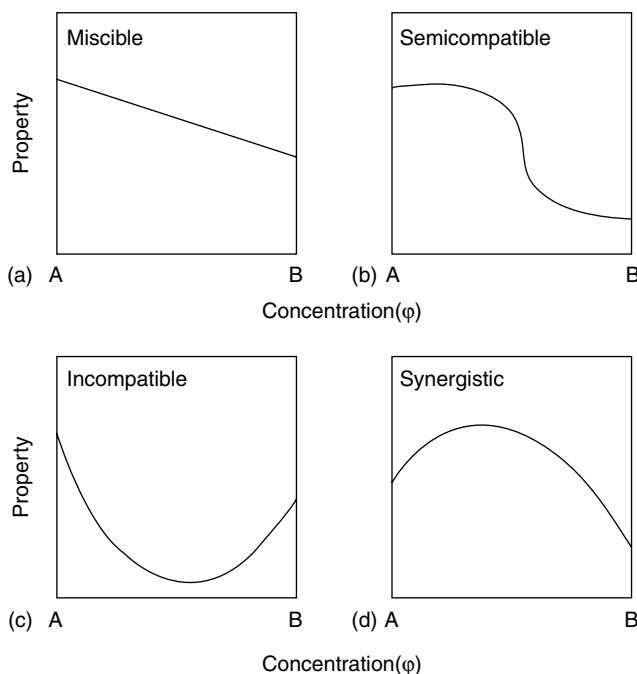


FIGURE 4.40 Properties vs. concentration of polymer components in a polyblend.

composition will be S-shaped showing an intermediate transition region where there is a phase inversion from one continuous phase to the other (Figure 4.40b). Most commercial polyblends are of this type, with the major polymer forming the continuous phase and retaining most of its useful properties, while the minor polymer forms small discrete domains, which contribute synergistically to certain specific properties.

When the polymer components in a blend are less miscible, phase separation will form larger domains with weaker interfacial bonding between them. The interfaces will therefore fail under stress and properties of polyblends are thus likely to be poorer than for either of the polymers in the blend. U-shaped property curves (Figure 4.40c) thus provide a strong indication of immiscibility. In most cases they also signify practical incompatibility, and hence lack of practical utility.

A fourth type of curve for properties vs. polyblend composition representing synergistic behavior (Figure 4.40d) has been obtained in a few cases of polymer blending. This shows improvement of properties, beyond what would be expected from simple monotonic proportionality, and sometimes far exceeding the value for either polymer alone. Synergism may result from a very favorable dipole-dipole attraction between the polymer components.

A blend of low-density polyethylene (LDPE) with the terpolymer ethylene-propylene-diene monomer rubber (EPDM) exhibits a synergistic effect on tensile strength if EPDM is partially crystalline, but a nonsynergistic effect if the EPDM is amorphous [65]. This example shows the dramatic effect that morphology can have on properties of polymer blends. The synergism apparently arises from a tendency for crystallites in the LDPE to nucleate crystallization of ethylene segments in the EPDM.

Stereochemistry is also important in determining properties of polyblends. For example, syndiotactic poly(methyl methacrylate) is miscible with poly(vinyl chloride) at certain concentrations, whereas the isotactic form is immiscible over the entire composition range [66].

4.3.12.1 Prediction of Polyblend Properties

A major problem in polyblend development is trying to predict polymer miscibility. The incompatibility of various pairs of polymers has been correlated with the mutual effects on intrinsic viscosities and dipole moment differences of the component polymers [67,68]. These results can give a guide for finding compatible polymer or polymer pairs or with very low incompatibility.

The viscometric study of the ternary system, that is, polymer A—polymer B—solvent, has been used in order to determine the interaction parameter χ_{AB} which characterizes the incompatibility of the couple polymer A—polymer B [60].

The viscometric study has also led to a method of estimation of the incompatibility of the polymer without the need to evaluate χ_{AB} . This method evaluates the quantity $\Delta[\eta]_{AB}$ defined by

$$\Delta[\eta]_{AB} = (1/2)(\Delta[\eta]_A + \Delta[\eta]_B)\% \quad (4.4)$$

where $\Delta[\eta]_A$ is the decrease of the intrinsic viscosity of the polymer A by the presence of the polymer B in the solvent, given by

$$\Delta[\eta]_A = ([\eta]_A - [\eta]_{AB})/[\eta]_A \quad (4.5)$$

The decrease is due to the incompatibility existing between polymer A and polymer B. The quantity $\Delta[\eta]_B = ([\eta]_B - [\eta]_{BA})/[\eta]_B$ similarly gives the decrease of the intrinsic viscosity of polymer B due to the presence of polymer A in the solvent. The constant quantity of the polymer A or B in the mixture, solvent plus polymer, is always the same (typically $0.125 \times 10^2 \text{ g/cm}^3$). Then the quantity $\Delta[\eta]_{AB}$ given by Equation (4.4) expresses a measure of the incompatibility existing between polymer A and polymer B. A high value of $\Delta[\eta]_{AB}$ for a polymer pair indicates a high value of incompatibility and vice versa.

The incompatibility of polymer pairs has been correlated with the dipole moment μ of two polymers. As it is known, the value of μ of each polymer [69] is given per monomer repeating unit and is given by the relation $\mu = (\bar{\mu}^2 / \overline{DP}_n)^{1/2}$, where \overline{DP}_n is the number average degree of polymerization and $\bar{\mu}^2$ is the mean square dipole moment of the long-chain molecules.

The values of $\Delta[\eta]_{AB}$ and $\Delta\mu$ for several pairs of vinyl polymers drawn from polystyrene, poly(methyl methacrylate), poly(vinyl chloride) and poly(vinyl acetate) are given in Table 4.35. It is seen that when the dipole moment of polymer A is very close to the dipole moment of polymer B, the incompatibility of the mixture, polymer A—polymer B, is very low. In the contrary, a mixture of polymer A and polymer B presents a high incompatibility when the dipole moment of polymer A is too different from that of polymer B.

In the case of two polymers presenting a high value of the difference $|\mu_A - \mu_B|$, the dissimilarity is high and the monomers of each polymer give interactions of the type $\delta^- - \delta^+$ with other monomers that belong to the same polymer and this leads to the phase separation. In the contrary, in the case of two polymers presenting a very low value of the difference $|\mu_A - \mu_B|$, the dissimilarity is low and the monomers of each polymer give interactions with other monomers that belong to the same or to the other polymer indifferently; hence the polymers are compatible.

Attempts to predict miscibility using simple solubility parameters of the type described in Chapter 1 have been largely unsuccessful because strong dipolar interactions are not taken into account. The importance of these interactions has been demonstrated, for example, with miscible mixtures of poly(acrylic esters) and poly(vinyl fluoride), where the compatibility has been attributed to dipolar interactions of the type

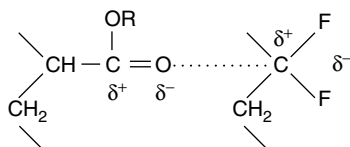


TABLE 4.35 Values of $\Delta[\eta]_{AB}$ and $\Delta\mu$ for Six Polymer Couples

Couples of Polymers	$\Delta[\eta]_{AB}$	$\Delta\mu$
PS–PMMA	7.00	0.99
PS–PVC	10.55	1.19
PS–PVA	11.20	1.34
PMMA–PVA	3.6	0.35
PMMA–PVC	10.55	1.19
PMMA–PVA	3.30	0.15

Predictions of properties for immiscible polyblends is much more complicated. This is partly due to the effects of varying morphologies that might arise as a result of processing variables. Frequently, one polymer will form a continuous phase with the second being dispersed as a noncontinuous phase in the form of spheres, lamellae, fibrils, and so on. It is, however, the polymer in the continuous phase that largely determines the properties of the polyblend.

For example, a 50:50 blend of polystyrene (a hard, glassy polymer at ordinary temperature) and polybutadiene (an elastomer) will be hard if polystyrene is the continuous phase, but soft if polystyrene is the dispersed phase. In some cases, however, an immiscible polyblend may have both components dispersed as continuous phases. Evidently, a proper control of phase morphology is of utmost importance with immiscible blends. The size of the dispersed phase should be optimized considering the final performance of the blend.

The major problem with immiscible blends is the poor physical attraction at phase boundaries that can lead to phase separation under stress resulting in poor mechanical properties. A number of ingenious approaches have been adopted to overcome this problem by improving compatibility between immiscible phases. One is through formation of interpenetrating polymer networks (IPN) as described in [Table 4.34](#).

In IPNs (discussed later) the polymers are physically “locked” together by the interdispersed three-dimensional network, a phenomena referred to as *topological bonding* [70]. Such mixtures, however, still undergo phase separation into microdomains that vary in size according to the degree of immiscibility. Kinetic control of phase separation during the formation of IPN [or the semi-interpenetrating polymer networks (SINs)] provides the method of generation of desired properties.

Another approach is to incorporate *compatibilizers* or interfacial agents into the blend to improve adhesion between phases. The concept of compatibilization of polymers is described in a later section.

4.3.12.2 Selection of Blend Components

The properties of engineering polymer blends and alloys that are sought to be improved by blending are impact strength, processability, tensile strength, rigidity/modulus, heat-deflection temperature, flame retardancy, thermal stability, dimensional stability, and chemical/solvent resistance. Among them, toughening and processability are of major concern. The second group of importance includes strength, modulus, and heat-deflection temperature, while the third group concerns flame retardancy, solvent resistance, as well as thermal and dimensional stability.

The patent literature also provides information on means of achieving these goals. As [Table 4.36](#) indicates, the blending effect in most case is nonspecific. Therefore, the data in Table 4.36 should only be considered as a general guide to blending. The fact that two polymers with desired properties are immiscible should, however, not be a deterrent since the modern compatibilization and reactive processing methods (discussed later) can overcome such problems.

The main reason for polymer blending is economy. If a material can be produced at a lower cost with properties meeting specifications, the manufacturer must use it to remain competitive. The main and most difficult task in polyblend production is the development of materials with a full set of desired

properties. This is usually achieved by selecting blend components in such a way that the principal advantages of one polymer will compensate for deficiencies of the second and vice versa. For example, the disadvantages of PPO with regard to processability and impact strength (see [Table 4.37](#)) are compensated by advantageous properties of either PA or HIPS. Due to PPO/PS miscibility, the original Noryls were formulated as PPO/HIPS polyblend.

The reactive methods of compatibilization developed subsequently allowed the second generation Noryl (a blend of PPO with PA) to be developed. The compositions claimed usually cover 30–70% of each of the main ingredients, PPO and PA, with additionally up to four parts of such modifier as polycarboxylic acid, trimellitic anhydride acid chloride, quinine, oxidized polyolefin wax, and so on. In most cases, PA forms a matrix with spherical inclusions of PPO acting as compatibilized low-density filler.

Similarly the disadvantages of PC are the stress cracking and chemical sensitivity. Stress cracking can be treated as a part of impact properties and a simple solution may thus be addition of ABS or ASA. On the other hand, to improve the solvent resistance—a property that is particularly important in automobile applications—a semicrystalline polymer may be added. From [Table 4.37](#), it is apparent that TPEs (e.g., PBT, PET) could provide that property, but they also lack warp resistance and impact strength. Hence an ideal blend for automobile application based on PC and TPEs should be impact modified with, for example, an acrylic latex copolymer. A schematic of preparation of this type of toughened blend introduced by GEC-Europe in 1979 under the tradename Xenoy is shown in [Figure 4.41](#).

As exemplified by PC/TPE/latex system, modern blends are increasingly required to play multiple roles so as to provide a balance of such diverse properties as mechanical behavior, chemical/solvent resistance, dimensional stability, paintability, weatherability, and, of course, economy. Such a complex balance is usually achieved by means of multicomponent blending often with unavoidable compromises.

4.3.12.3 Compatibilization of Polymers

Blends made from incompatible polymers are usually weak. These poor blends are a result of high interfacial tension and poor adhesion between the two phases. For many years, blending of polymers was unsuccessful due to the fact that many polymers were incompatible. Lately new polymer blends have been successfully made by the use of compatibilizing agents. This has yielded polymers of unique properties not attainable from either of the polymer components of the blends. Sometimes these blends

TABLE 4.36 How to Modify Properties by Blending

Property	Matrix Resin	Modifying Polymer
Impact strength	PVC, PP, PE, PC, PA, PPE, TPE	ABS, ASA, SBS, EPR, EPDM, PBR, SAN, SMA, MBA, polyolefin, HIPS
HDT, stiffness	PC, PA, ABS, SAN	TPEs, PEI, PPE PC, PSO
Flame retardancy	ABS, acrylics PA, PC	PVC, CPE Aromatic-PA, PSO, copolysiloxanes or phosphazanes
Chemical/solvent resistance	PC, PA, PPO	TPEs
Barrier properties	Polyolefins	PA, EVOH, PVCl ₂
Processability	PPO PET, PA, PC PVC PSO PO	Styrenics PE, PBR, MBS, EVOH CPE, acrylics PA PTFE, SI

For abbreviations see [Appendix A2](#).

Source: Utracki, L. A. 1989. *Polymer Alloys and Blends*. Hanser Publishers, Munich, Germany.

TABLE 4.37 Advantages and Disadvantages of Some Engineering Polymers and Modifiers

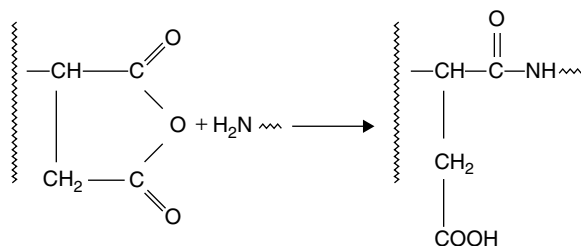
Polymer	Advantages in	Disadvantages in
Polyamide (PA)	Processability, impact strength, crystallinity	Water absorption, HDT
Polycarbonate (PC)	Low-temperature toughness, HDT	Stress-crack sensitivity, solvent and chemical resistance
Polyoxymethylene (POM)	Tensile strength, modulus	Stress-crack sensitivity, impact strength
Polyphenylene oxide (PPO)	HDT, rigidity, flame retardancy	Processability, impact strength
Thermoplastic polyesters (PET, PBT)	Chemical and solvent resistance	Shrinkage, low-temperature toughness, processability
High-impact polystyrene (HIPS)	Processability, impact strength	HDT
Acrylonitrile–butadiene–styrene copolymer (ABS or ASA)	Impact strength, processability, weatherability	HDT

Source: Utracki, L. A. 1989. *Polymer Alloys and Blends*. Hanser Publishers, Munich, Germany.

are preferred over completely miscible blends since they may combine important characteristics of both polymers. Their performance greatly depends on the size and morphology of the dispersed phase.

Polymers can be compatibilized in a number of ways. Polymers that act as mutual solvents can be used as compatibilizing agent, e.g., polycaprolactone in a blend of polycarbonate and poly(styrene-*co*-acrylonitrile).

Polymers can also be compatibilized by the use of functionalized polymers. Thus polymers can be post-reacted with a reactive monomer to form functional groups that react with a second polymer to form grafts in a blend, e.g., EPDM-*g*-maleic anhydride/nylon-6,6 blends are produced by grafting maleic anhydride onto EPDM, followed by blending with nylon-6,6. The grafted maleic anhydride reacts with the terminal—NH₂ groups of the nylon to form the following copolymer:



This method allows us to generate the compatibilizer in situ during blending (e.g., by adding benzoyl peroxide and maleic anhydride to EPDM followed by nylon in a twin screw extruder) and is often called *reactive blending* or *reactive compatibilization*. Block or graft copolymers can also be added separately to produce blends with controlled particle sizes. This type of compatibilizing agent is called an interfacial agent since it acts at the boundary between two immiscible polymers.

An interfacial compatibilizing agent functions as surfactant, somewhat the same as low molecular weight surfactant used in emulsion polymerization. It is usually a block or graft copolymer and is located at the interface between two polymers (Figure 4.42). It reduces interfacial tension, alleviates gross segregation, and promotes adhesion. The effective concentrations are from 0.1% to 5% depending on the desired particle size and the effectiveness of the compatibilizing agent.

The block or graft copolymer used as a compatibilizing agent must have the ability to separate into their respective phase and not be miscible as a whole molecule in one phase. The best choice of block or graft copolymers would be to choose polymers identical to the blended polymers, e.g., poly(A-*b*-B) or poly(A-*g*-B) copolymers for blending poly(A) and poly(B). Another alternative is to use poly(C-*b*-D) or

poly(C-g-D) where C and D are compatible with A and B, respectively or where C and D adhere to A and B, respectively, but are not miscible with them.

Examples of such compatibilized systems that have been studied include EPDM/PMMA blends compatibilized with EPDM-g-MMA, polypropylene/polyethylene blends with EPM or EPDM, polystyrene/nylon-6 blends with polystyrene/nylon-6 block copolymer, and poly(styrene-co-acrylonitrile)/poly(styrene-co-butadiene) blends with butadiene rubber/PMMA block copolymer.

Reactive compatibilizing agents of the type A-C can also compatibilize an A/B blend as long as C can chemically react with B. Such studied systems include polyethylene (PE)/nylon-6 blends compatibilized with carboxyl functional PE, polypropylene (PP)/poly(ethylene-terephthalate), with PP-g-acrylic acid, nylon-6,6/EPDM with poly(styrene-co-maleic anhydride), and nylon-6/PP with PP-g-maleic anhydride.

In several commercial polymer blends, “modifiers” that also act as compatibilizing agents are used. The modifier is usually an interactive copolymer containing a rubbery component. Acrylic-based copolymers, chlorinated polyolefins, ethylene-propylene-diene, poly(ethylene-co-vinyl acetate), etc., are frequently used. These play a dual role, compatibilizing and toughening the blend. For this reason, they are used at much higher loading than pure compatibilizers. Thus, while 0.1–5 wt% of the latter may be sufficient, 10–40 wt% of a modifier may be needed (see Figure 4.41).

Co-reaction of blends to improve the performance has for decades been a practice in the rubber industry. In high-shear mixers some of the chains in rubbers are broken and are reformed by the free-radical mechanism. A similar phenomenon occurs during intensive mixing of polyolefins (see Table 4.34). To enhance this process, sometimes a free-radical source, e.g., peroxides, can be added.

4.3.12.4 Industrial Polyblends

The automotive sector is an important area for polymer blends. Alloys of polycarbonate (PC) and poly(butylenes terephthalate) (PBT), which combine the high impact strength of PC with the resistance of gasoline and oil and processing ease of PBT, are being increasingly used in car bumpers. General Electric's PC/PBT alloy is used for bumpers in several cars made in the United States and Europe. Bayer's PC/PBT blends, called Makrolon PR, are used for several automobile impact-resistant parts. Makrolon EC900 is also used for crash helmets.

An important requirement for plastics materials in the automotive industry is paintability alongside metal components in high temperature areas. Noryl GTX series of General Electric has been developed to meet this requirement. The blend consisting of polyphenylene oxide (PPO) in a nylon matrix combines the heat and dimensional stability and the low water absorption of PPO with the flow and semicrystalline properties of nylons. Its impact strength, however, is not as high as PC/PBT blends.

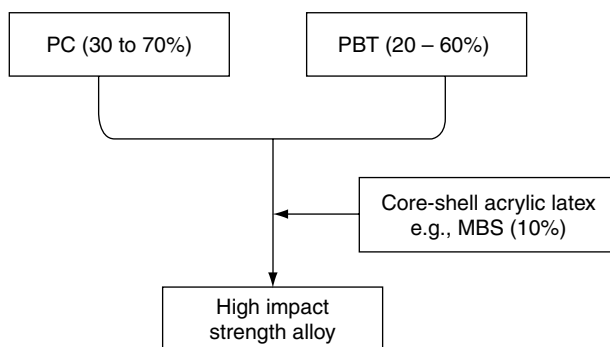


FIGURE 4.41 Schematic of preparation of polycarbonate/poly(butylenes terephthalate) blend. (After Utracki, L. A. 1989. *Polymer Alloys and Blends*. Hanser Publishers, Munich, Germany.)

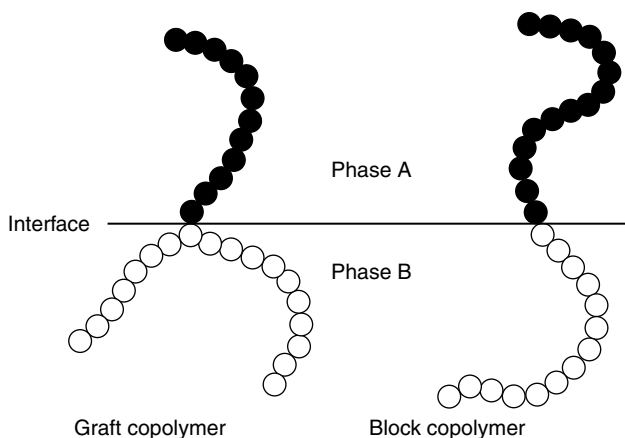


FIGURE 4.42 Ideal location of block and graft copolymers at the interface between polymer phases A and B in a polyblend.

Several grades of Noryl GTX are available, some of these being glass-filled. The unfilled grades are used for automobile exterior components such as fenders, spoilers and wheeltrims, whereas the glass-reinforced grades are used in under-the-bonnet applications, such as cooling fans, radiator end caps, and impeller housings, where in addition to high heat resistance extra stiffness is required.

Bayer's Bayblend PC/ABS alloys are used in dashboard housings, interior mirror surrounds, and steering column covers. The high stability of the alloy allows pigmentation in pastel colors.

Some alloys of PPO have been developed specifically for office equipment and housings. Noryl AS alloys, which are blends of PPO/PS and special fillers, are expected to replace metals in such applications as structural chassis for typewriters and printers.

Monsanto Chemical Co. produce injection molded Nylon/ABS alloys (Triax) that are characterized by good toughness, high chemical resistance, and easy moldability. Applications of these alloys include industrial power tools, lawn and garden equipment housing and handles, gears, pump impellers, and car fascia.

Bayer and BASF have developed a PC/ASA blend where ASA is the rubber variant of ABS in which the polybutadiene phase is completely replaced by a polyacrylate rubber. Compared to PC/ABS alloys, the PC/ASA blend has greater resistance to weathering, which permits outdoor applications and an extra heat stability that reduces the risk of yellowing in processing. BASF's alloy, Terblend S, is recommended for outdoor applications as it has six times the UV resistance of PC/ABS and an even higher resistance when pigmented.

A number of polyphenylene ether (PPE) blends have been introduced by Borg-Warner, Huls, and BASF. These blends have the advantage that they can be made flame retardant without halogens. Borg-Warner offers many grades of PPE/high impact polystyrene (HIPS) blend under the trade name PreveX. The materials are characterized by high impact resistance and high heat distortion temperature. Applications are for office equipment, business machines, and telecommunication equipment. Luranyl PPE/HIPS blends of BASF include general purpose types, reinforced grades, impact modified types, and flame-proof blends. BASF also has a PPE/nylon blend tradenamed Ultranyl, which is aimed at a similar market.

Blends have also been used to a limited extent in packaging. Du Ponts Solar is a nylon/polyethylene blend that can be blow-molded into bottles and can contain volatile hydrocarbons found in household cleaners and agricultural chemicals. Further developments in such barrier blends are expected.

A number of commercial blends are listed in [Appendix A13](#) indicating their compositions, properties, and typical uses.

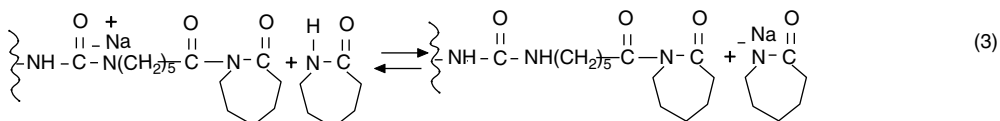
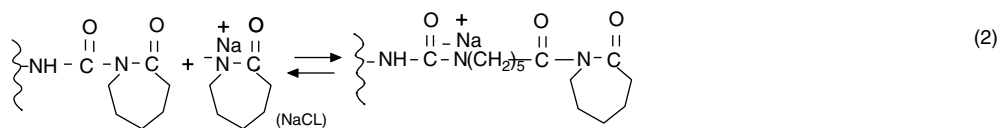
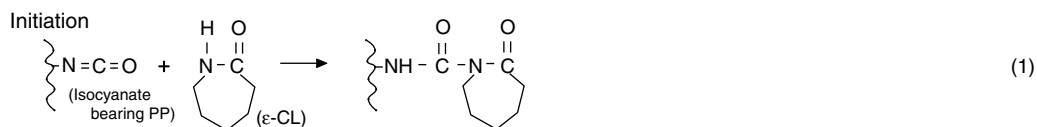
4.3.12.5 Nanoblends

For most polymer blends processed under typical extrusion conditions, the particle size of the dispersed phase is rarely below 0.1 μm (or 10 nm), whatever the compatibilization method employed [71]. Recently, however, a novel extrusion process involving an in situ polymerizing and compatibilizing system has been reported [72] for the preparation of nanostructured blends (*nanoblends*). [By nanoblends it is meant that the scale of dispersion of one polymer phase in the other is below 100 nm.] The method essentially consists of polymerizing a monomer of polymer A in the presence of polymer B, while a fraction of polymer B chains bears initiating sites at the chain ends or along the chain backbones from which polymer A chains can grow. In the process, polymer A and a graft or block copolymer of A and B are formed simultaneously, leading to in situ polymerized and in situ compatibilized A/B polymer blends [73]. The feasibility of such a process has been demonstrated by synthesizing nanoblends of polypropylene (PP)/polyamide-6 (PA-6) [72].

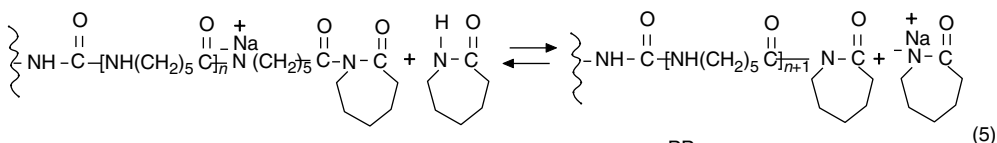
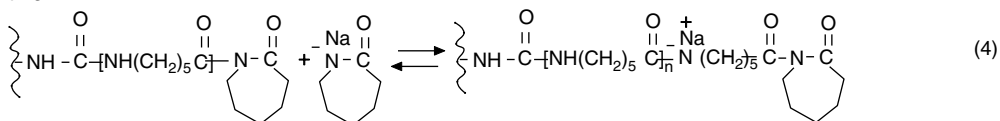
In a typical method to synthesize PP/PA-6 nanoblends, the monomer ϵ -caprolactam (ϵ -CL) is polymerized in the matrix of PP, a fraction of the latter having 3-isopropenyl- α,α -dimethylbenzene isocyanate (TMI) grafted on it to act as centers for initiating PA-6 chain growth. As such, the formation of PA-6 homopolymer and a graft copolymer of PP and PA-6 takes place simultaneously in the matrix of PP, leading to compatibilized PP/PA-6 blends, with the dispersed phase (PA-6) particle size between 10 and 100 nm that cannot be achieved otherwise by melt-blending pre-made PP and PA-6. The underlying chemistry of the process is shown in [Figure 4.43](#).

Anionic polymerization of ϵ -CL in the presence of a catalyst (sodium caprolactamate, NaCL) and an activator (such as an isocyanate) yields PA-6. In the reaction scheme shown in [Figure 4.43](#), the TMI-grafted PP (denoted by PP-g-TMI) acts as the macroactivator as it has isocyanate groups hanging from the polymer chain. (It should be noted that, unlike classical isocyanates, TMI with an isocyanate group is sufficiently stable under extrusion conditions involving high temperature and exposure to moisture.) Basically, polymerization starts with the formation of an acyl caprolactam as a result of the reaction between $\text{N}=\text{C}=\text{O}$ and ϵ -CL (reaction 1). This acyl caprolactam then reacts readily with NaCL forming a new reactive sodium salt (reaction 2). As the latter initiates the polymerization of ϵ -CL, the catalyst (NaCL) is regenerated (reaction 3). Repetition of reactions 2 and 3 finally leads to the formation of a PA-6 chain grafted to PP (propagation reactions 4 and 5). Similar steps involving a microactivator, such as $\text{R}-\text{N}=\text{C}=\text{O}$, also result in the formation of PA-6 homopolymer. This simultaneous formation of PA-6 and graft copolymer of PP and PA-6 in the PP matrix, when the system PP-g-TMI/ ϵ -CL/NaCL/ $\text{R}-\text{N}=\text{C}=\text{O}$ is used, results in a well stabilized PP/PA-6 nanoblend. As compared to this, if ϵ -CL is polymerized only in the presence of PP, as in the system PP/ ϵ -CL/NaCL/ $\text{R}-\text{N}=\text{C}=\text{O}$, a highly immiscible mixture of PP and PA-6 will be obtained with morphology quite similar to that obtained by simply blending PP and PA-6 polymers. PP/PA-6 nanoblends cannot also be obtained by reactive blending in a system such as PP-g-MA (maleic anhydride grafted PP)/PA-6.

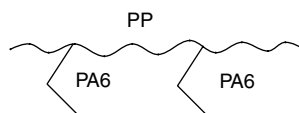
The mechanism of copolymer formation in the PP-g-TMI/ ϵ -CL/NaCL/ $\text{R}-\text{N}=\text{C}=\text{O}$ system is quite different from that in the PP-g-MA/PA-6 system. In the latter, the interfacial region surrounding a PA-6 particle is composed of the PP-g-MA and PA-6 bearing a terminal amine group (see [Figure 4.44a](#)). Their reaction at the interfaces leads to the formation of a graft copolymer PP and PA-6. The amount of copolymer formed by this method is limited primarily by the total interfacial volume [74], which is very small compared to the bulk. The situation, however, is very different for the PP-g-TMI/ ϵ -CL/NaCL/ $\text{R}-\text{N}=\text{C}=\text{O}$ system. Being immiscible with the PP-g-TMI, the mixture of ϵ -CL/NaCL/ $\text{R}-\text{N}=\text{C}=\text{O}$ is in the form of fine droplets in the PP-g-TMI. The interfacial region surrounding a droplet of ϵ -CL/NaCL/ $\text{R}-\text{N}=\text{C}=\text{O}$ is PP-g-TMI/ ϵ -CL/NaCL (see [Figure 4.44b](#)). The polymerization of ϵ -CL occurs in these droplets leading to PA-6 particles, which are stabilized by a layer of the graft copolymer resulting from the polymerization of PP-g-TMI/ ϵ -CL/NaCL in the interfacial region. In this case, the problem of interfacial volume is no longer important for copolymer formation which depends largely on the capacities of the PP-g-TMI (macroactivator) and $\text{R}-\text{N}=\text{C}=\text{O}$ (microactivator) to initiate ϵ -CL. If the amount of the microactivator is zero, one would obtain a pure PP-g-PA-6 graft copolymer. It is the capacity of the in situ



Propagation:



Expected structure of the graft
copolymer of PP and PA-6 formed :



Molecular structure of 3-isopropenyl- α , α -dimethylbenzyl isocyanate (TMI)

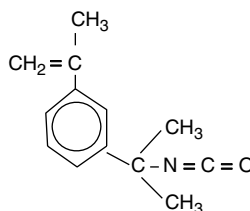


FIGURE 4.43 Schematic description of the mechanism of formation of a graft copolymer of PP and PA-6 using an isocyanate bearing PP, such as TMI-grafted PP (PP-g-TMI) as macroactivator. The mechanism of polymerization of ε -CL can be described by the same sequence of steps 1–5 with the macroactivator replaced by a microactivator $\text{R}-\text{N}=\text{C}=\text{O}$. (After Hu, G. H., Cartier, H., and Plummer, C. 1999. *Macromolecules*, 32, 4713. With permission.)

polymerization and in situ compatibilization process to generate very high amounts of copolymer that allows the formation and stabilization of nanodispersion [72].

4.3.13 Interpenetrating Polymer Networks

An interpenetrating polymer network (IPN) has been defined [75,76] as “an intimate combination of two polymers both in network form, at least one of which is synthesized or cross-linked in the presence of the other.” There are no induced covalent bonds between the two polymers, i.e., monomer A reacts only with other molecules of monomer A.

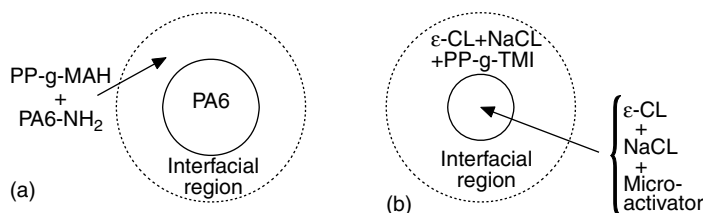


FIGURE 4.44 Comparison of the mechanism of copolymer formation in (a) conventional reactive blending of PP/PA-6 system with PP-g-MAH as compatibilizer which reacts with -NH_2 end groups of PA-6 and (b) *in situ* polymerizing and compatibilizing system (see text). (After Hu, G. H., Cartier, H., and Plummer, C. 1999. *Macromolecules*, 32, 4713. With permission.)

A schematic representation of an ideal IPN (*full IPN*) in which both the polymers are cross-linked is shown in Figure 4.45a. If one of the two polymers is in network form (cross-linked) and the other a linear polymer, i.e., not cross-linked, the product is called a *semi-IPN* (Figure 4.45b).

An IPN is distinguished from simple polymer blends and block or graft copolymers in two ways: it swells but does not dissolve in solvents, and creep and flow are suppressed [75].

IPNs represent a third mechanism, in addition to mechanical blending and copolymerization, by which different polymers can be intimately combined. IPNs can be synthesized either by sequential polymerization or simultaneous polymerization of two monomers. In a sequential synthesis, monomer I is polymerized using an initiator and a cross-linking agent to form network I. Network I is then swollen in monomer II containing cross-linking agent and initiator to form network II by polymerization *in situ*. Such polymers are called *sequential interpenetrating networks* (SIPN).

Polymer networks synthesized by mixing monomers or linear polymers (prepolymers) of the monomers together with their respective cross-linking agents and catalysts in melt, solution, or dispersion, followed, usually immediately, by simultaneous polymerization by noninterfering modes, are called *simultaneous interpenetrating networks* (SIN). In the latter process, the individual monomers are polymerized by chain or stepwise polymerization, while reaction between the polymers is usually prevented due to different modes of polymerization.

Interpenetrating polymerization is the only way of combining cross-linked polymers. This technique can be used to combine two or more polymers into a mixture in which phase separation is not as extensive as it would be otherwise. Normal blending or mixing, it may be noted, result in a multiphase morphology unless the polymers are completely compatible. However, complete compatibility, which is almost impossible, is not necessary for complete phase mixing by interpenetrating polymerization, since permanent entanglements produced by interpenetration prevent phase separation.

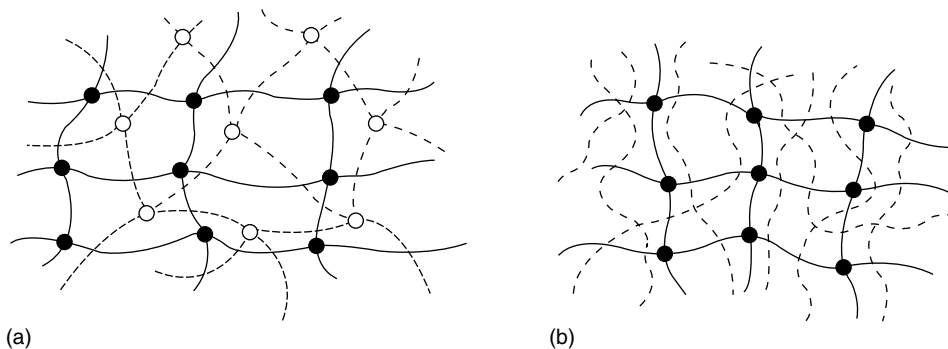


FIGURE 4.45 Schematic representation of (a) a full IPN and (b) a semi-IPN.

With moderate compatibility, intermediate and complex phase behavior results. Thus IPNs with dispersed phase domains have been reported ranging from a few micrometers (the largest) to a few hundred nanometers (intermediate) to those without a resolvable domain structure (complete mixing). With highly incompatible polymers, on the other hand, the thermodynamics of phase separation is so powerful that it occurs before it can be prevented by cross-linking.

Combining polymeric networks in different compositions often results in IPNs with controlled different morphologies showing synergistic behavior. For example, a glassy polymer (T_g above room temperature) combined with an elastomeric polymer (T_g below room temperature) gives a reinforced rubber, if the elastomeric phase is predominant and continuous, or a high impact plastic, if the glassy phase is continuous. More complete phase mixing enhances mechanical properties due to increased physical cross-link density. IPNs have thus been synthesized in various network compositions with optimum bulk properties such as tensile strength, impact strength, and thermal resistance.

4.3.13.1 Industrial IPNs

Commercial IPNs have been developed to combine useful properties of two or more polymer systems. For example, high levels of silicone have been combined with the thermoplastic elastomer (TPE) based on Shells Kraton styrene–ethylene/butadiene–styrene TPE and Monsanto Santoprene olefin TPE. These IPN TPEs are said to provide the biocompatibility and release properties of silicone with tear and tensile strength up to five times greater than medical-grade silicone. Thermal and electronic properties and elastic recovery are also improved.

IPN TPEs offer physical and thermal properties of thermoset rubber, the processability of a thermoplastic, and a wider hardness range than available to other TPEs.

Rimplast materials from Petrarch are silicone/thermoplastic IPNs that combine the warpage and wear resistance properties of silicone with nylon, thermoplastic polyurethane, or styrene/butadiene block copolymers. The combination of properties these IPNs possess make them suitable for high quality, high tolerance gear and bearing applications that can benefit from the addition of internal lubrication and isotropic shrinkage of silicone to the fatigue endurance and chemical resistance of crystalline resin, while processability still remains the same.

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5

Polymers in Special Uses

5.1 Introduction

There are a number of polymeric materials that distinguish themselves from others by virtue of their limited use, high prices, or very specific application or properties. The expression specialty polymer is, however, slightly ambiguous to use for such materials as the definition covers any polymeric material that does not have high volume use. There are thus some materials that were originally developed as specialties have now become high volume commodities, while a number of materials developed some years ago still fall into the specialty category. Some examples of the latter are polytetrafluoroethylene, polydimethyl siloxane, poly(vinylidene fluoride), and engineering materials such as poly(phenylene oxide), poly(phenylene sulfide) (PPS), polyether sulfone, polyether ether ketone, and polyetherimide.

In this chapter, attention is focused on a number of polymers that are either themselves characterized by special properties or are modified for special uses. These include high-temperature and fire-resistant polymers, electroactive polymers, polymer electrolytes, liquid crystal polymers (LCPs), polymers in photoresist applications, ionic polymers, and polymers as reagent carriers and catalyst supports.

5.2 High-Temperature and Fire-Resistant Polymers

Compared to traditional materials, especially metals, organic polymers show high sensitivity to temperature [1–3]. Most importantly, they exhibit very low softening points, which is attributed to the intrinsic flexibility of their molecular chains. Thus, whereas most metals do not soften appreciably below their melting points, which may be 1000°C or higher, many polymers commonly used as plastics such as polyethylene, polystyrene, and poly(vinyl chloride), soften sufficiently by about 100°C to be of no use in any load-bearing applications.

The poor thermal resistance of common polymers has greatly restricted some of their application potential. In two particular application areas, namely electrical and transport applications, this restriction has long been particularly evident.

Owing to their unique electric insulation properties, polymers are widely used in electrical products. However, many electrical components are required to operate at high temperatures, for example, electric motors and some domestic appliances.

Another characteristic property of polymers, namely their high specific stiffness and strength (which are due to their low density, especially when used in fiber-reinforced composite materials), has led to the use of polymers in transport applications, especially in aerospace industries, where weight saving is of vital importance and materials cost is secondary. However, here again many applications also demand high temperature resistance.

Road vehicle manufacturers in their attempt to save weight (and hence reduce fuel consumption) have been replacing heavy metal components with light plastic ones. The ease of molding plastics into intricately shaped part has also been used to advantage for fabricating many under-the-bonnet products. Here again, resistance to elevated temperatures is often also needed, necessitating use of high-temperature resistant polymers.

Although electrical and transport applications have perhaps provided the biggest demand for thermally resistant specialty polymers, such polymers are also sought for use in more mundane consumer goods, especially appliances where exposure to elevated temperature can occur, such as hair dryers, toasters, and microwave ovens.

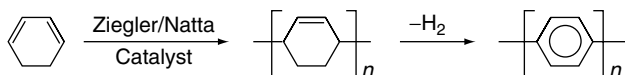
5.2.1 Temperature-Resistant Polymers

To measure the thermal stability of polymers, one must define the thermal stress in terms of both time and temperature. An increase in either of these factors shortens the expected lifetime. In general terms, for a polymer to be considered thermally stable, it must retain its physical properties at 250°C for extended periods, or up to 1000°C for a very short time (seconds). As compared to this, some of the more common engineering thermoplastics such as ABS, polyacetal, polycarbonates, and the molding grade nylons have their upper limit of use temperatures (stable physical properties) at only 80°C–120°C.

The principal ways to improve the thermal stability of a polymer are to increase crystallinity, introduce cross-linking, increase inherent stiffness of the polymer chain, and remove thermoxidative weak links. Although cross-linking of oligomers is certainly useful and does make a real change in properties (see [Chapter 1](#)), crystallinity development has limited application for very high temperatures, since higher crystallinity results in lower solubility and more rigorous processing conditions. Chain stiffening or elimination of weak links is a more fruitful approach.

The weakest bond in a polymer chain determines the overall thermal stability of the polymer molecule. The aliphatic carbon–carbon bond has a relatively low bond energy (see Table 5.1). Oxidation of alkylene groups is also observed during prolonged heating in air. Thus the weak links to be avoided are mostly those present in alkylene, alicyclic, unsaturated, and nonaromatic hydrocarbons. On the other hand, the functions proven to be desirable are aromatic (benzenoid or heterocyclic) ether, sulfone, and some carboxylic acid derivatives (amide, imide, etc.). Aromatic rings in the polymer chain also give intrinsically stiff backbone.

It follows from this reasoning that aromatic polymers will have greater thermal stability. For example, poly(*p*-phenylene) synthesized by stereospecific 1,4-cyclopolymerization of cyclohexadiene, followed by dehydrogenation:

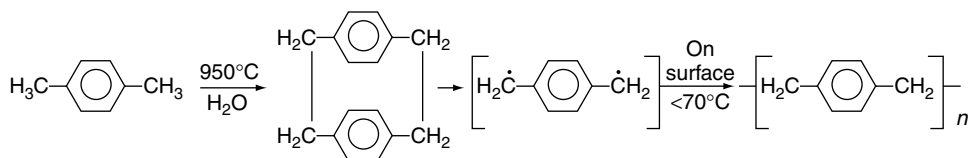


is infusible and insoluble.

TABLE 5.1 Bond Energies of Common Organic and Inorganic Polymers

Bond	Bond Energy	
	(kcal/mol)	(kJ/mol)
C _{al} –C _{al}	83	347
C _{ar} –C _{ar}	98	410
C _{al} –H	97	405
C _{ar} –H	102	426
C–F	116	485
B–N	105	439
Si–O	106	443

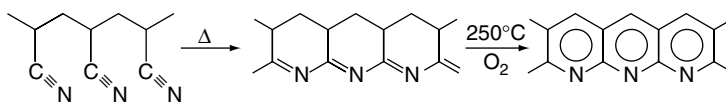
Another example of aromatic polymer is poly(*p*-xylene), which is usually vacuum deposited as thin films on substrates. In one application the monomer is di-*p*-xylylene formed by the pyrolysis of *p*-xylylene at 950°C in the presence of steam. When this monomer is heated at about 550°C at a reduced pressure, a diradical results in the vapor phase, which, when deposited on a surface below 70°C, polymerizes instantaneously and forms a thin, adherent coating.



Metals or other substrates can be coated in this way. A major application has been the production of miniature capacitors that have the polymer as a dielectric.

Commercial polymers based on the principle of synthesis of polyaromatic compounds include the previously discussed commercial polymers—aromatic polyamides, polyimides, poly(phenylene oxide), polysulfone, and polybenzimidazole (see Chapter 4).

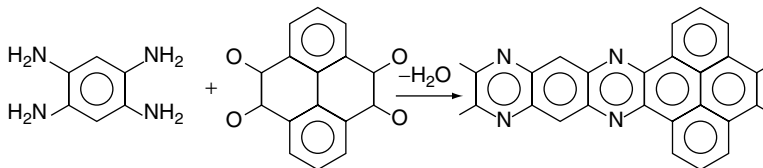
Another approach to achieve thermal stability is to synthesize ladder polymers, so called because of their ladderlike structure (□□□□). For example, pyrolysis of polyacrylonitrile given a ladder polymer of high thermal stability:



The product (black orlon) is so stable that it can be held directly in a flame in the form of woven cloth and not be changed physically or chemically. Further heating of black orlon to 1400°C–1800°C and simultaneous stretching produces graphite HT. If the heating and stretching is conducted at 2400–2500°C, the high modulus graphite HM is obtained. Other carbonizable polymers that produce carbon fibers on heating include poly(vinyl acetate), poly(vinyl chloride), poly(vinylidene chloride), and cellulose. Thermosets, such as phenolic resins, generally produce nongraphitizing or glassy carbon.

Ladder polymers are also produced by polycondensation reactions of tetrafunctional monomers. If a tetrafunctional monomer is reacted with a bifunctional monomer, as in the formation of polyimides, the derived polymer is referred to as a partial ladder or stepladder polymer.

If two tetrafunctional monomers are used, as in the formation of polyquinoxaline (PQ) from an aromatic tetramine and an aromatic tetraketone, the resulting polymer is a ladder polymer:



Other tetraketones have also been used in the preparation of PQs. The PQs have proven to be one of the better high temperature polymers with respect to both stability and potential application. The PQs are also one of the three most highly developed systems—the others being benzimidazoles and oxadiazoles. The interest in the PQs increased considerably after the development in 1967 of the soluble phenylated polyquinoxaline (PPQ). PQs are stable to 550°C and are used for high-temperature composites and adhesives.

5.2.2 Fire-Resistant Polymers

To understand the burning of polymers better, the combustion region may be divided into five zones, as shown in Figure 5.1. The first zone is defined by the polymer layer where pyrolysis takes place due to heat produced in the flame, but very little oxidation takes place. Thermal oxidation takes place in the second superficial zone. In the third zone, which is a gaseous one, low-molecular-weight products formed in these two zones are mixed with heated air and are decomposed or oxidized by oxygen or by radicals coming out of the flame.

The fourth zone begins where the concentration of degradation products is sufficient for the flame to grow, emitting light radiation. This is where most of the thermal energy is released, and the temperature reaches its maximum value. The fifth zone, also called the post-combustion zone, is where oxidation reactions terminate and combustion products are found in maximum concentration. The thermal energy produced in this zone and in the fourth zone, together with the light radiation, are responsible for the degradation that occurs in the inner part of the polymer not touched by the flame.

It is evident from the above discussion that the burning of polymers may be considered to consist of three principal stages, namely, (1) thermal (nonoxidative) decomposition of the polymer, (2) evolution and transport of volatiles from the burning surface to the flame, and (3) high temperature (600°C–900°C) oxidation of the volatiles in the flame itself. Interruption of the processes occurring at any of the above three stages will reduce polymer flammability. Thus, polymers with good thermal stability that are, therefore, resistant to thermal decomposition also offer good fire resistance.

Although, because many factors are involved, no single test can provide an adequate picture of the fire hazards of polymers, the limiting oxygen index (LOI) is the single most widely used test of polymer flammability. The test (ASTM D-2863) is made in a very simple way. A small rod of a plastic material is burned in a Pyrex tube in the presence of oxygen and nitrogen (see Figure 3.83). The tubing is connected to flowmeters and the minimum amount of oxygen, in an oxygen–nitrogen mixture, required to just sustain burning is determined. The LOI is defined by

$$\text{LOI} = \frac{[\text{O}_2]}{[\text{O}_2] + [\text{N}_2]} \times 100$$

Thus a smaller LOI value indicates a greater flammability. LOI values for some common and not so common polymers are shown in Table 5.2.

The polymers listed in Table 5.2 have been classified into non-self-extinguishing and self-extinguishing types depending on their LOI values.

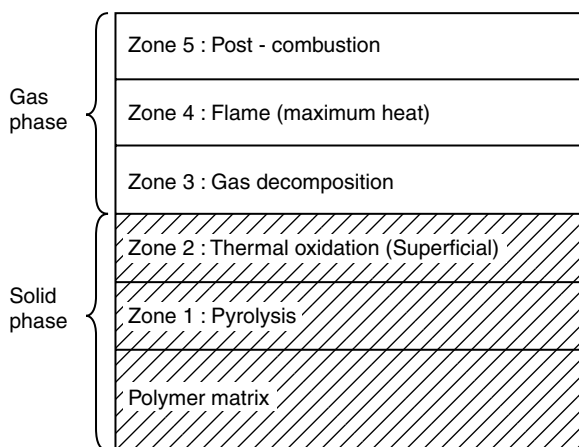


FIGURE 5.1 Schematic representation of the combustion region of a burning polymer.

TABLE 5.2 Limiting Oxygen Indices (LOI) of Polymers

Non-Self-Extinguishing Polymer	LOI	Self-Extinguishing Polymer	LOI
Polyoxymethylene	16	Polycarbonate	27
Polyethylene	17	Polyarylate	34
Polypropylene	18	Polyethersulfone	38
Polystyrene	18	Polyether ether ketone	40
Poly(methyl methacrylate)	18	Poly(vinyl chloride), rigid	42
Polyisoprene (natural rubber)	18	Polyamide-imide	43
ABS	18	Poly(phenylene sulfide)	44
Nylon-6,6	24	Polyether-imide	47
Poly(ethylene terephthalate)	25	Polypyromellitimide	50
Polychloroprene	26	Poly(vinylidene chloride)	60
		Polytetrafluoroethylene	95

The LOI value for self-extinguishing behavior is often taken as 27, not 21 (which is the volume % concentration of oxygen in air), to correct for a lack of convective heating in the LOI test.

It is seen that aromatic polymers have low flammability and are self-extinguishing, which reflects their much greater thermal stability compared with aliphatic polymers. It is because of this property that aromatic polymers are often specified in fire-hazardous electrical insulation applications or for fire-resistant textiles. In contrast, most of the common polymers, with the exception of PVC, are non-self-extinguishing and flammable.

The presence of halogen in a polymer produces the most dramatic increase in LOI and decrease in flammability. Thus, rigid (unplasticized) PVC, with a LOI value of 42, has the lowest flammability of any common and many not so common polymers. This advantage is, however, offset by the large amount of smoke and toxic gas (hydrochloric acid) produced when PVC and other chloropolymers burn. Moreover, plasticization of PVC markedly reduces the LOI; for example, the value decreases to 25 when 50 phr dioctylphthalate is used as a plasticizer.

Fluoropolymers also low flammability. The fully fluorinated polymer polytetrafluoroethylene, for example, burns only in 95% oxygen under the test conditions of LOI. The burning, however, produces a highly toxic and corrosive gas hydrogen fluoride.

5.3 Liquid Crystal Polymers

Ordinarily a crystalline solid melts sharply at a single, well-defined temperature to produce a liquid phase that is amorphous and isotropic. A different behavior is exhibited by a class of organic compounds known as liquid crystals. The oldest examples are cholesterol derivatives, e.g., cholesteryl benzoate. This substance, for instance, does not have a sharp transition to amorphous liquid at 145.5°C, but changes to a cloudy liquid, which becomes clear and isotropic only at 178.5°C. This cloudy intermediate state that possesses an ordered structure with some resemblance to a crystalline solid, while still in the liquid state, is called a mesophase or mesomorphic phase from the Greek *mesos*, meaning in between or intermediate.

Liquid crystal materials can thus be defined as those which are characterized by the appearance of mesophases between the crystalline solid and isotropic liquid phases. Many organic compounds with this property have been synthesized. The temperature range of stability of a mesophase may be anything up to 150°C.

Liquid crystals can be divided into two main classes; those forming liquid crystalline phases in the melt are called thermotropic and those forming liquid crystalline phase in solution are referred to as lyotropic. Depending on the type of molecular order in the mesophase these classification can be broken down further into three main categories: smectic, nematic, and cholesteric [4–7].

Smectic liquid crystals consist of elongated molecules that line up with the long axes of the molecules aligned in one direction and the ends of the molecules lying on parallel planes to produce a type of layered structure (Figure 5.2a) like that in a layered box of cigars. A layer of smectic molecules is just one molecule (longitudinally) thick. The molecules in nematic liquids are similar in shape to smectic molecules and also point in one direction, but unlike the latter they do not line up with the ends lying on parallel planes (Figure 5.2b).

Cholesteric liquid crystals consist of long flat molecules that line up in the same manner as nematic molecules with molecular long axes parallel to each other in a plane. However, the molecules in one plane are slightly displaced (due to side groups of molecules) with respect to those in the neighboring planes to form a helical pattern, as indicated Figure 5.2c. Since the cholesteric structure is basically a derivative of the nematic, a transition from the cholesteric structure to the nematic structure can be effected by using a magnetic or electric field to unwind the helical configuration of the former.

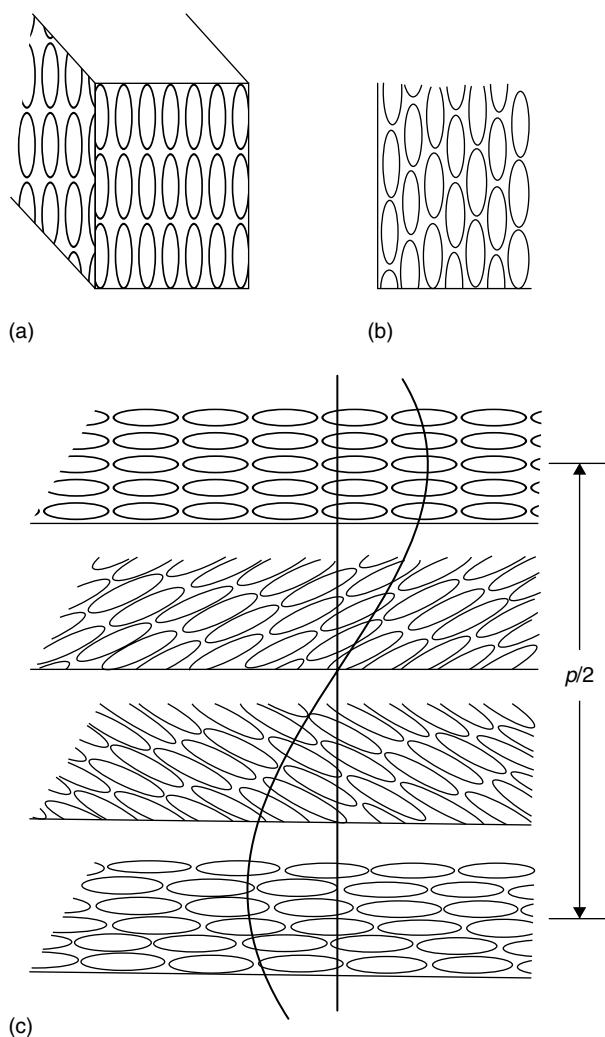


FIGURE 5.2 Liquid crystals. (a) Smectic crystals: the ends of the molecules are on a plane. (b) Nematic crystals: the ends of the molecules do not match. (c) Cholesteric crystals: the molecules in each layer are arranged in a manner similar to nematic crystals, but the angle changes from plane to plane of the molecules, forming a helix of pitch length p .

Liquid crystals have interesting electro-optical properties. When subjected to small electric fields, reorientation and alignment of the liquid crystal molecules takes place, which produces striking optical effects because light travels more slowly along the axes of the molecules than across them. This has led to their use in optical display devices for electronic instruments such as digital voltmeters, desk calculators, clocks, and watches. Nematic liquid crystals are most commonly used in these applications. Cholesteric materials are added to provide memory effects.

Molecules that have a tendency to form liquid crystalline phase usually have either rigid, long rod-like shapes with a high length to breadth (aspect) ratio, or disc-shaped molecular structures. These rigid groups, referred to as mesogens, may be chemically composed of a central core comprising aromatic or cycloaliphatic units joined by rigid links, and having either polar or flexible alkyl and alkoxy terminal groups.

Polymers exhibiting liquid crystalline properties can be constructed from these mesogens in three different ways: (1) incorporation into chain-like structures by linking them together through both terminal units to form main-chain LCPs; (2) attachment through one terminal unit to a polymer backbone to produce a side-chain comb-branch structure; and (3) a combination of both main- and side-chain structures. LCPs typically show either smectic or nematic liquid crystal behavior. A schematic diagram of the two main phase types is shown in Figure 5.3.

The liquid crystalline phases in polymeric materials are sometimes difficult to identify unequivocally. However, several techniques can be used that provide information on the nature of the molecular organization within the phase, and if used in a complimentary fashion these can provide reliable information on the state of order of the mesogenic groups.

While differential scanning calorimetry is widely used as a means of detecting the temperatures of thermotropic mesophase transitions, the phases can be identified by observing the characteristic textures developed in thin layers of the polymer when viewed through a microscope using a linearly polarized light source. X-ray diffraction can be used to characterize the mesophases and to provide reliable information on the number of phases present.

The type of phase formed in a polymer liquid crystal can also be identified often by examining the manner in which it mixes with a small molecule mesogen of known mesophase type. If these textures are the same, then a mixed liquid crystal phase is formed with no observable transition between the two types of molecule.

In some polymer crystals, moreover, several mesophases can be identified. In main-chain LCPs there is usually a transition from the crystal to a mesophase, while in more amorphous systems where a glass

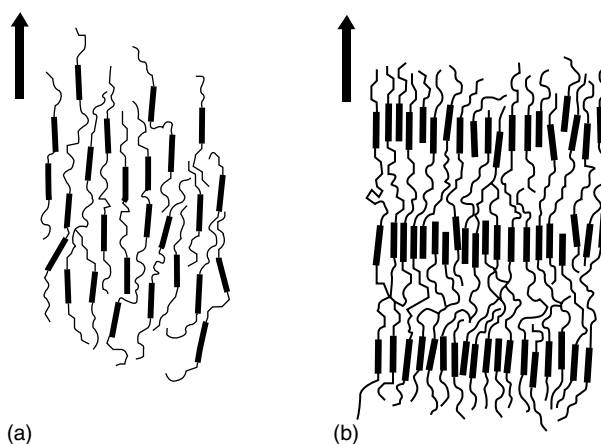
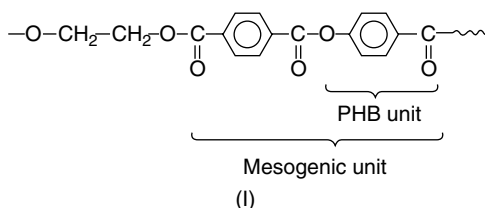


FIGURE 5.3 Schematic representation of (a) nematic phase and (b) smectic phase for main-chain liquid crystalline polymers, showing the director as the arrow. The relative ordering is the same for side-chain-polymer liquid crystals.

transition (T_g) is present, the mesophase may appear after this transition has occurred. In thermotropic system having multiphase transitions, the increase in temperature leads to changes from the most ordered to the least ordered states, i.e., crystal \rightarrow smectic \rightarrow nematic \rightarrow isotropic (see Figure 5.4).

From the standpoint of polymer applications, two properties of LCPs are of major interest—the effect of order on polymer melt viscosity, and the ability of the polymer to retain its ordered configuration when cooled down to the solid state.

Among the first polymers observed to exhibit the aforesaid properties of LCPs were copolyesters (I) prepared from terephthalic acid, ethylene glycol, and *p*-hydroxybenzoic acid



As the amount of *p*-hydroxybenzoate (PHB) units is increased, the polymer melt viscosity initially increases, which is expected because of the decreased flexibility caused by incorporation of the “rigid” PHB unit. At levels of 30 mol% PHB, however, the melt viscosity begins to decrease, reaching a minimum at about 60–70 mol%. This is shown in Figure 5.5a at three different shearing rates. Significantly, as the melt viscosity begins to decrease, the melt’s appearance also changes from clear to opaque.

Both the decrease in viscosity and appearance of opacity arise from the onset of liquid crystalline morphology, which in turn is due to increased backbone rigidity. The rigid polymeric mesophases become aligned in the direction of flow, thus minimizing the frictional drag. Liquid crystal melts or solutions have, in consequence, lower viscosities than melts or solutions of random-coil polymers. The significance of this effect from the standpoint of polymer processing is obvious: the lower the viscosity, the more readily the polymer can be fabricated into a useful plastic or fiber.

An equally important observation for the above copolyester LCPs is that the ordered arrangement of polymeric mesophases in the melt is retained upon cooling, which is manifested in greatly improved mechanical properties (see Figure 5.5b). The liquid crystalline behavior is therefore advantageous from the standpoint of both processing and properties. Thermotropic liquid crystal copolyesters of structures similar to (I) are now available commercially.

Ordered behavior is also observed in solutions of some liquid crystal polymers (lyotropic LCPs). Unlike flexible polymers that assume a random coil conformation in solution, the rigid polymers being

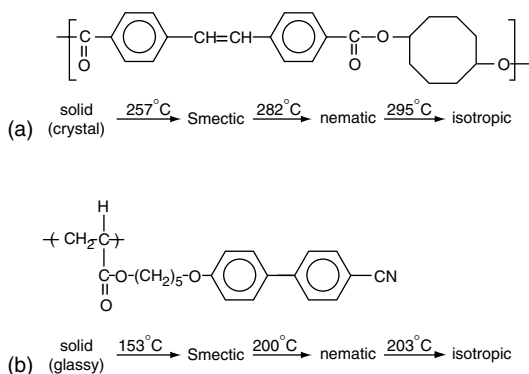


FIGURE 5.4 Examples of thermotropic liquid crystal polymers showing multiphase transitions: (a) main-chain polymer; (b) side-chain polymer.

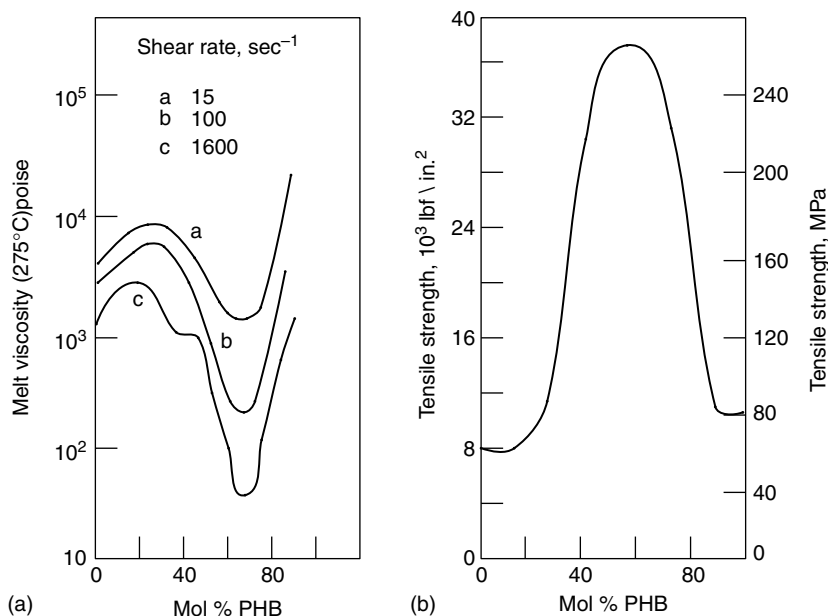


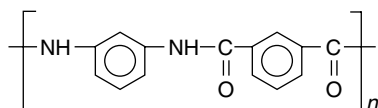
FIGURE 5.5 Effect of *p*-hydroxybenzoic acid concentration on (a) melt viscosity and (b) tensile strength of a terephthalic acid/*p*-hydroxybenzoic acid/ethylene glycol copolyester. (After Lenze, R. W. and Lin, J. I. 1986. *Polym. News*, 11, 200.)

rod-like tend to cluster together in bundles of quasi-parallel rods as their concentration in solution increased. These form domains that are anisotropic and within which there is nematic order of the chains. There is, however, no directional correlation between the domains themselves unless the solutions are shared. When shearing takes place the domains tend to become aligned parallel to the direction of flow, thereby reducing viscosity of the system.

Lyotropic LCPs exhibit quite characteristic viscosity behavior in solution as the polymer concentration in solution is changed. Typically the viscosity follows the trend shown in Figure 5.6. As more and more polymer is added to the solvent, the viscosity increases while the solution remains isotropic and clear. At a critical concentration (which depends on the polymer and the solvent) the solution becomes opaque and anisotropic and there occurs a sharp fall in viscosity with further increase in the polymer concentration. This results from the formation of oriented nematic domains in which the chains are now aligned in the direction of flow, thereby reducing the frictional drag on the molecules.

The additional chain orientation in the direction of the fiber long axis, obtained from the nematic self-ordering in the system, leads to a dramatic enhancement of the mechanical properties of the polymer. A number of aromatic polyamides have thus achieved commercial importance because of the very high tensile strengths and moduli of the fibers that can be spun from the nematic solutions. These have consequently become attractive alternatives to metal or carbon fiber for use in composites as reinforcing material. The most significant of these aramid fibers are:

1. Poly(*m*-phenylene isophthalamide), trade name Nomex



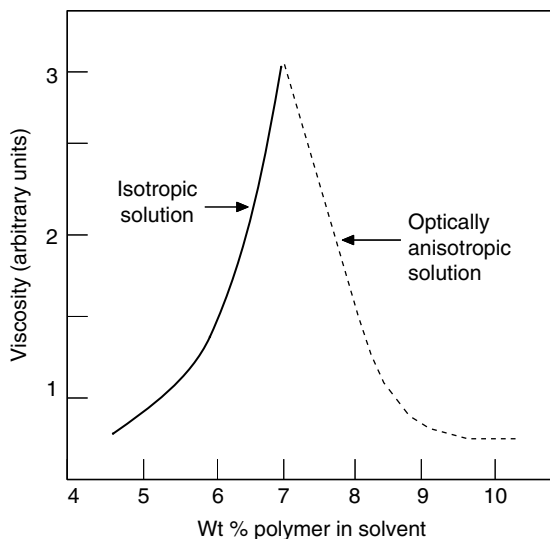
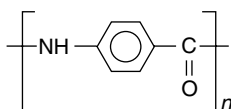
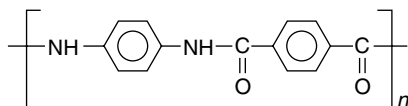


FIGURE 5.6 Variation of viscosity of solutions of partially chlorinated poly(1,4-phenylene-2,6-naphthalamide) dissolved in solvent mixture of hexamethylene phosphoramidate and *N*-methylpyrrolidone containing 2.9% LiCl, as a function of solution concentration showing transition from isotropic to anisotropic behavior. (After Morgan, P. W. 1979. *Chem. Tech.*, 316.)

2. Poly(*p*-benzamide) or Fiber B



3. Poly(*p*-phenylene terephthalamide), trade name Kevlar



The last-named polymer exhibits liquid crystalline phase in sulfuric acid solution. The solution is extruded to form a fiber, resulting in further alignment of the molecules. The product, once the sulfuric acid is removed, is a fiber with a more uniform alignment than could be obtained simply by drawing and thus has much better mechanical properties. Tensile strength of Kevlar (see [Table 4.17](#)), for example, is considerable higher than that of steel, whereas its density is much lower. Although most Kevlar produced is used in tie cord, the polymer also finds use in specialty clothing. Light-weight bulletproof vests are made containing up to 18 layers of woven Kevlar cloth.

LCPs have significantly increased crystalline melting temperatures as a result of the extended chain morphology. In fact, major drawbacks to the type of rigid polymers that exhibit liquid crystalline behavior are that they have a very high melting point—e.g., poly(*p*-hydroxybenzoic acid) melts at about 500°C—and are difficult, if not impossible, to dissolve in the usual organic solvents. This makes them difficult to process, so alternative structures with much lower melting points are more useful.

The melting points of LCPs can be reduced in a number of different ways (schematically represented in [Figure 5.7](#)), namely,

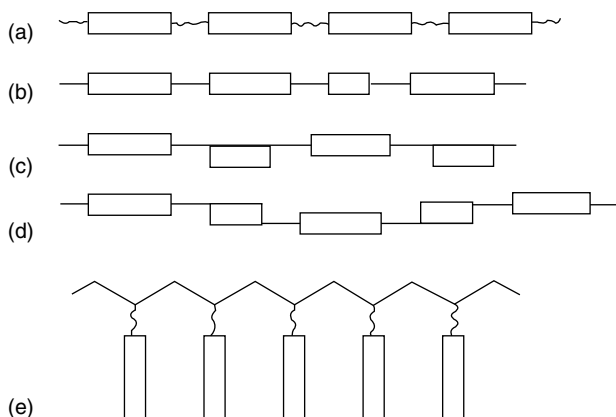


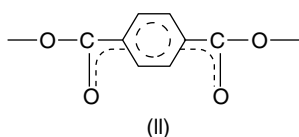
FIGURE 5.7 Schematic representation of several arrangements of mesogens (□) and flexible spacers (∼) in main chain and side chain of liquid crystalline polymers.

1. Incorporation of flexible spacer units, e.g., $-(CH_2)_n-$, $-(CH_2-CH_2-O)_n-$, $-S-R-S-$, and $-(SiR_2-O)_n-$ in chain to separate the rigid backbone groups (mesogens), which are responsible for the mesophases (Figure 5.7a).
2. Copolymerization of several mesogenic monomers of different sizes to give a random and more irregular structure (Figure 5.7b).
3. Introduction of kinks in the main chain, such as by using meta substituted monomers (Figure 5.7c) or a crankshaft monomer (e.g., 6-hydroxy-2-naphthoic acid) (Figure 5.7d).
4. Attachment of mesogens to the polymer backbone via flexible spacers (Figure 5.7e).

5.3.1 Thermotropic Main-Chain Liquid Crystal Polymers

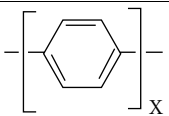
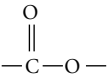
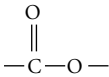
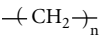
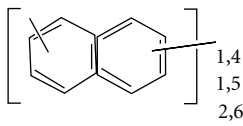
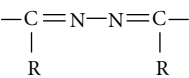
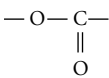
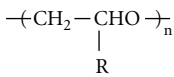
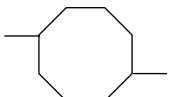
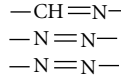
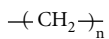
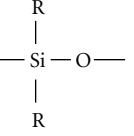
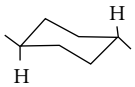
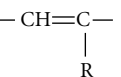

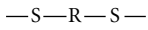
The use of flexible spacers is a popular approach for producing thermotropic main-chain polymer liquid crystals. The mesogenic moiety consists of two cyclic units, normally joined by a short rigid bridging group. These are then linked through functional groups to flexible spacers of varying length that separate the mesogens along the chain and thus reduce the overall rigidity. The schematic chemical constitution of these main chain LCPs, together with example of the various types of groups that have been used are shown in Table 5.3.

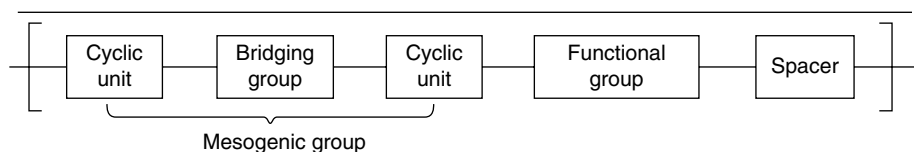
The bridging groups are usually multiple bond units, because they must be rigid to maintain the overall stiffness of the mesogens. Ester groups also serve this purpose, particularly when the cyclic units are aryl rings where the conjugation leads to a stiffening of the overall structure (II):



Many of the examples of thermotropic main-chain LCPs are polyesters that are synthesized by condensation reactions including interfacial polymerizations, or by high-temperature solution polymerizations using diols and diacid chlorides. However, the preferred method is often an ester interchange reaction in the melt. Among the commonly used monomer units are *p*-hydroxybenzoic acid, terephthalic acid, 2,6-naphthalene dicarboxylic acid, 2-hydroxy-6-naphthoic acid, and 4,4'-biphenol. The main-chain LCPs prepared in this way, however, tend to be very insoluble polymers with high melting points and mesophase ranges that make them difficult to process. A common approach is thus to introduce flexible

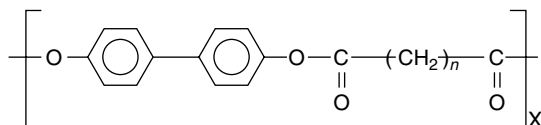
TABLE 5.3 Chemical Constitution Typical of Thermotropic Main-Chain-Polymer Liquid Crystals, i.e., [4]

Cyclic Unit	Bridging Group	Functional Group	Spacer
 $X = 1-3$			
			
			
			

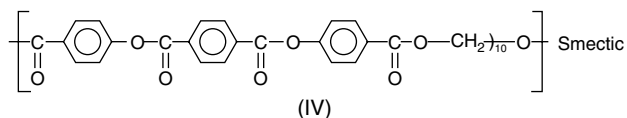
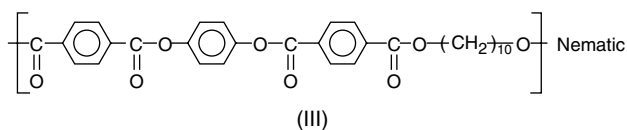


spacers in order to obtain more tractable LCPs (Table 5.3). The spacer units are usually introduced by a copolymerization reaction and the proportion of the spacer units relative to the mesogens can be varied resulting in alteration of the melting point and the temperature range of mesophase.

The majority of the main chain LCPs having group arrangements as shown in Table 5.3 exhibit a nematic phase after melting, but in some cases small variations in structure can lead to formation of a smectic mesophase. Thus for polyesters with the following structures:



A nematic phase is observed when the number of methylene units (n) in the spacer is odd, but a smectic mesophase results when n is even. Similarly, for polyesters with multiple rings, the phases can be nematic or smectic depending on the orientation of the ester units, e.g., (III) and (IV):



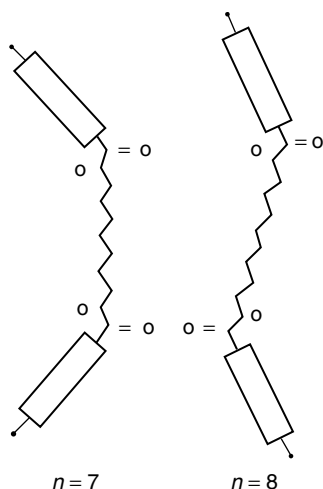


FIGURE 5.8 Schematic diagram showing the effect of odd and even number of $-\text{CH}_2-$ spacer units on the relative orientation of the mesogenic units in a main-chain liquid crystal polymer. (After Krigbaum, W. R., Watanabe, J., and Ishikawa, T. 1983. *Macromolecules*, 16, 1271.)

enced by the flexibility of the backbone chain and whether the mesogen is attached directly to the chain or is separated from the chain by a flexible spacer unit.

The degree of flexibility of the polymer chain to which the mesogens are bonded can affect both the glass transition temperature (T_g) and the mesophase to isotropic phase transition temperature (T_i). This is illustrated in Table 5.4 for a number of side-chain LCPs having the same mesogen. The temperatures of the transitions are seen to decrease with the increase in chain flexibility, the latter being in the order methacrylate < acrylate < siloxane. The thermal range of the mesophase (ΔT) is thus the greatest when the chain is most flexible and its conformational changes largely do not interfere with, or disrupt, the anisotropic alignment of the mesogens in the liquid crystalline phase.

The influence of the polymer backbone on the alignment of the side-chain mesogens can be minimized by decoupling the motions of the main chain from those of the mesogens. This can be achieved by introducing long flexible spacer units between the backbone and the mesogen. A typical side-chain LCP structure would thus be that shown at the top of Table 5.5. Structures of this type can be synthesized in a number of ways. One such scheme is shown in Figure 5.9.

It is generally observed that as longer spacer units are introduced, the T_g of the polymer is lowered by internal plasticization and the tendency for the more ordered smectic phase to develop is increased. A similar ordering effect is also encouraged by lengthening the alkyl tail unit (see Table 5.7). Both these phenomena reflect the known tendency for long side chain to order and eventually to crystallize, when sufficiently long, and this condition persists also in the liquid crystal state.

The ordered state of the mesophase in the aforesaid crystalline polymers is readily frozen and locked into a glassy state if the temperature is rapidly brought down below the T_g and remain stable until heated above T_g again. The phenomenon offers several interesting application possibilities in optoelectronics and information storage (discussed latter). These applications often depend on the ability of the mesogenic groups to align under the influence of an external magnetic or electric field, as discussed below.

As the dielectric constant and diamagnetic susceptibility of many mesogens are anisotropic, the orientation of side-chain LCPs in the nematic state can also be changed by the application of a magnetic

The length of the spacer unit has significant effect on the melting point (T_m) and isotropic transition temperature (T_i), and hence on the temperature range ($T_i - T_m$) in which the meso-phase is stable.

Polymers with spacers having an even number of CH_2 units usually have higher melting (T_m) and clearing (T_i) temperatures than those with an odd number. This suggests that the spacer length influences the ordering in the liquid crystal phase. As shown schematically in Figure 5.8, it is easier with even-numbered methylene unit spacers to maintain the orientation of the mesogen parallel to the director axis in the all *trans* zig-zag conformation.

5.3.2 Side-Chain Liquid Crystal Polymers

It has been demonstrated that polymers with mesogens attached as side chains can exhibit liquid crystalline properties. The extent to which mesophases can develop in these system is influ-

TABLE 5.4 Effect of Chain Flexibility on the Transition Temperatures of Side-Chain Liquid Crystal Polymers Having a Common Mesogen [4]

Polymer	Transitions (°C)	ΔT (°C)
$\left[\text{CH}_2 - \underset{\text{COOR}}{\overset{\text{CH}_3}{\text{C}}} \right]_n$	Glassy $\xrightarrow{-187}$ Nematic $\xrightarrow{201}$ Isotropic	14
$\left[\text{CH}_2 - \underset{\text{COOR}}{\text{CH}} \right]_n$	Glassy $\xrightarrow{-160}$ Nematic $\xrightarrow{177}$ Isotropic	17
$\left[\text{O} - \underset{\text{CH}_2\text{R}}{\overset{\text{CH}_3}{\text{Si}}} \right]_n$	Glassy $\xrightarrow{-142}$ Nematic $\xrightarrow{168}$ Isotropic	26
$\text{R} = \text{---}(\text{CH}_2)_2\text{---O---} \langle \text{benzene ring} \rangle \text{---C(=O)---O---} \langle \text{benzene ring} \rangle \text{---O---CH}_3$		

of electric field. The parameter of interest is the magnitude of the critical field, which is required to affect transition (Fredericks transition) from the homogeneous to the homeotropic aligned state (see Figure 5.10).

Whereas the relaxation time for this transition in low-molecular-weight mesogens is of the order of seconds, this may be several orders of magnitude larger in polymer systems due to viscosity effects. Though this makes the use of polymeric liquid crystals less attractive in rapid-response display devices, the additional stability that can be gained in polymeric systems can be distinctly advantageous for some applications as thermorecording in optical storage systems.

The principles of using side-chain LCPs as optical storage systems have been demonstrated using a polymer film prepared from a side-chain polymer with the structure as shown in Figure 5.4b. The mesogenic side groups are first oriented by application of an electric field to the polymer above its T_g , such that homeotropic alignment is obtained. On cooling below the T_g , the alignment is locked into the glassy phase, and a transparent film that will remain stable on removal of the electric field is produced. If a laser beam is now used to address the film, localized heating occurs at the point where the beam impinges on the film and the material passes into the isotropic, disordered, melt state. This results in a local loss of the homeotropic orientation at the place of laser exposure and, on cooling, an unoriented region with a polydomain texture, which scatters light and thus produces a nontransparent spot, forms in the film (see Figure 5.11). Information can thus be “written” onto the film, and can subsequently be erased by simply raising the temperature of the whole film to regain the isotropic, disordered, melt state.

5.3.3 Chiral Nematic Liquid Crystal Polymers

Cholesteric mesophase (Figure 5.2c) is a special form of nematic phase, first observed in low-molecular-weight esters of cholesterol. This structure can often be detected in mesogenic systems containing a chiral center and hence is also called the chiral nematic state. The structure, as shown in Figure 5.2c, is a helically disturbed nematic phase, where each alternate layer is displaced by an angle θ relative to its immediate neighbors, thus imparting a helical twist (with a pitch p) to the phase. A system with this type of ordering has very high optical activity and an ability to selectively reflect circularly polarized light of a

TABLE 5.5 Schematic Representation of the Organization of a Side-Chain Liquid Crystal Polymer (SCLCP) [4]

SCLCP \equiv Flexible backbone — Functional unit — Spacer — Functional unit — Cyclic unit — Bridging group — Cyclic unit — Flexible tail					
Flexible Backbone	Functional Unit	Spacer	Cyclic Unit	Bridging Group	Flexible Tail
$-\text{CH}-\text{CHR}-$ 	None	None	$\left[\text{C}_6\text{H}_4 \right]_{1,3,1,4}$	None	None
$-\text{SiR}-\text{O}-$ 	$-\text{O}-$	$-(\text{CH}_2)_n-$	$\left[\text{C}_6\text{H}_4 \right]_{1,3,1,4}$ X=Me Ph Cl	$-\text{CO}-\text{O}-$	R
$-\text{SiR}-\text{O}-\text{SiR}_2-\text{O}-$ 	$-\text{CO}-\text{O}-$	$-(\text{CH}_2-\text{CHR})_n-$	$\left[\text{C}_6\text{H}_4 \right]_{n=1,2,3}$	$-\text{CR}=\text{CR}-$	OR
$-\text{P}=\text{N}-$ 	$-\text{O}-\text{CO}-$	$-\text{NR}'-\text{R}-\text{NR}'-$	$\left[\text{C}_{10}\text{H}_6 \right]_{1,4,1,5,2,6}$	$-\text{C}\equiv\text{C}-$	CN
		$-\text{S}-\text{R}-\text{S}-$	(Cholesteryl)	$-\text{CR}=\text{NO}-$	
		$-\text{SiR}_2-\text{O}-$		$-\text{NO}=\text{N}-$	
				$-\text{CR}=\text{N}-\text{N}=\text{CR}-$	

Source: Cowie, J. M. G. 1991. *Polymers: Chemistry and Physics of Modern Materials*. Blackie, Glasgow and London.

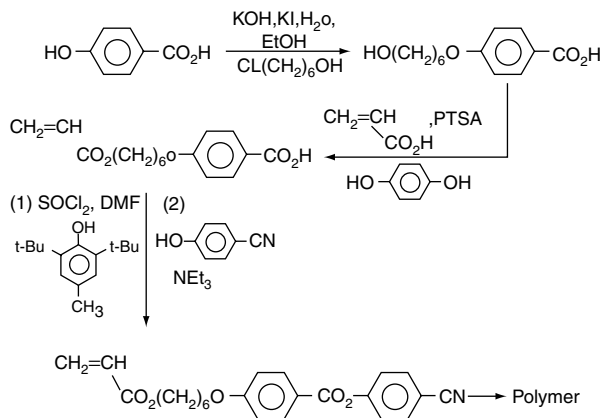


FIGURE 5.9 A representative scheme of synthesis of side-chain liquid crystal polymer of the type shown in Table 5.5. The monomer containing the mesogenic unit is first synthesized and then polymerized to obtain the liquid crystal polymer.

specific wavelength, when irradiated by normal light. The wavelength (λ_R) of this reflected light is related to the pitch p of the helical structure by

$$\lambda_R = np \quad (5.1)$$

where n is the average refractive index of the liquid crystalline phase.

The chiral nematic state, first observed in cholesteryl derivatives, was later detected in other chiral mesogens, and can also be induced by adding small chiral molecules to a host nematic LCP. Chiral nematic LCPs have thus been synthesized as side-chain polymers by introducing a chiral unit in the tail moiety of mesogens or by copolymerizing cholesterol-containing monomers with another potential mesogenic monomer. Examples [4] of these types are shown as structures (V) and (VI):

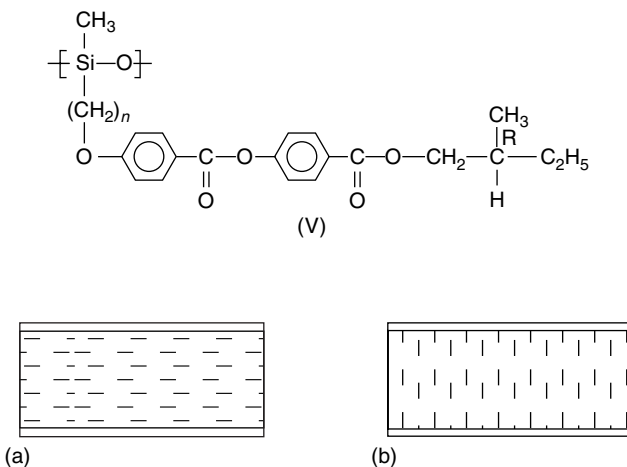
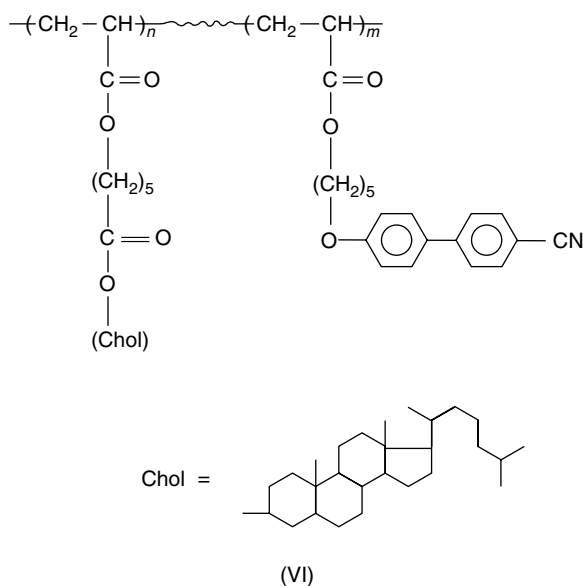


FIGURE 5.10 Schematic representation of (a) homogeneous and (b) homeotropic alignment of mesogens in a measuring cell. (After Folmer, B. J. B., Sijbesma, R. P., Versteegen, R. M., Van der Rijt, J. A. J., and Meijer, E. W., 2000. *Adv. Mater.*, 12, 874. With permission.)



The data in Table 5.6 indicate that as the content of the chiral monomer (cholesterol) is varied in the copolymer, the wavelength of the reflected light (in the average temperature region between T_g and T_i) changes. This suggests that the composition changes alter the pitch (p) of the helical structure in the chiral nematic phase, with consequent changes in the reflected light wavelength [see Equation 5.1]. For (VI), the increase in cholesterol content apparently causes the helix twist to become tighter, i.e., p becomes smaller and so λ_R moves to shorter wavelengths. The pitch is also sensitive to temperature. When the temperature is raised, the helix tends to unwind (i.e., p increases) with a consequential increase in λ_R .

Like the other side-chain LCPs described in the previous section, these materials also offer the possibility of locking the chiral nematic phase into the glassy state by rapid cooling to temperatures below T_g . This leads to a preservation of the structure and its reflected color. With suitable systems, the process can thus be used to produce stable and light-fast monochromatic films.

5.3.4 Properties of Commercial LCPs

The first LCP to be launched commercially was Dartco's Xydar, introduced in 1984 [11]. Xydar injection-molding resins are aromatic polyesters based on terephthalic acid, p -hydroxybenzoic acid, and p,p' -dihydroxybiphenyl. Xydar has a high melting point (close to 400°C), which necessitates certain modifications to processing equipment. It also has a high melt viscosity making it difficult to mold in

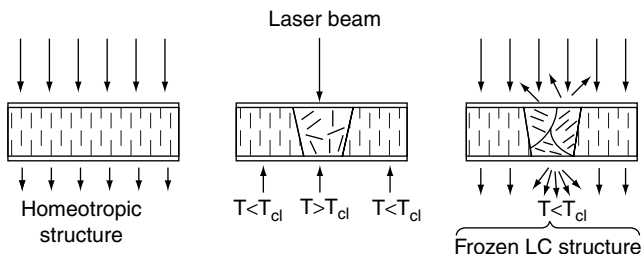


FIGURE 5.11 Thermal recording using a homeotropically aligned side-chain liquid crystal polymer as a transparent film. A laser beam is used to address the film by producing local heating and disorder, which is subsequently frozen in by cooling. (After Folmer, B. J. B., Sijbesma, R. P., Versteegen, R. M., Van der Rijt, J. A. J., and Meijer, E. W., 2000. *Adv. Mater.*, 12, 874. With permission.)

TABLE 5.6 Variation of λ_R with Copolymer Composition for Structure (VI) [4]

% Chol	T_g (°C)	T_i (°C)	λ_R (nm)
34	10	32	850
40	10	39	660
55	13	40	555
65	13	65	500

Source: Cowie, J. M. G. 1991. *Polymers: Chemistry and Physics of Modern Materials*. Blackie, Glasgow and London.

small sections. An advantage of Xydar, however, is that it offers high retention of mechanical properties even at temperatures in excess of 300°C.

A second range of LCPs were introduced by Hoechst Celanese under the trade name Vectra. Vectra is an aromatic polyester condensate derived from 2,6-dihydroxynaphthalene. Its main advantages are its fast cycling and ease of processing, the melt temperature for both injection and extrusion grades being typically about 285°C.

Cycle time of Vectra can be less than half that of other engineering plastics, i.e., on the order of 530 sec depending on part design. This is due to a number of factors. Since the melt is already ordered, parts require little or no crystallization time. LCPs moreover have an exceptionally low heat of transition; so little heat of crystallization must be removed, thereby allowing for fast cooling. And because compounds have excellent stiffness at high temperatures, parts are stiff enough to eject without cooling.

The material is noncorrosive to molds and clean running, while its exceptionally low melt viscosity ensures easy filling of complex, small-part geometries. No modifications are required to processing equipment. However, as with filled or reinforced polymers, tools should be hardened to minimize the effects of abrasion.

Vectra LCPs consist of parallel, closely packed, fibrous chains in injection molded parts which give the polymer a wood-like appearance at fracture surfaces and also give it self-reinforcing properties that are at least as good as those of conventional fiber-reinforced thermoplastics. ICI supplies LCPs (self-reinforcing polymers) under the trade name Victrex SRP. Excellent physical properties, low combustibility and smoke generation, resistance to chemicals and solvents, and stability towards radiation are some of the important properties of LCPs.

LCPs being anisotropic, their properties are enhanced along with the direction of flow and decreased across the flow direction. This anisotropic ratio is reduced by the presence of fillers, which is in contrast to conventional polymer composites. Thus the properties of fiber-filled LCPs, such as shrinkage, modulus, and creep, are less anisotropic than those of the unfilled LCP. These LCPs also retain their excellent mechanical properties when used for long periods of time at elevated temperatures.

Because of the low melt viscosity of LCPs, thin sections can be molded with highly filled (70%) LCPs. The addition of bulk lubricants reduces the melt viscosity. Injection molded parts are produced with a minimum of molded-in stress, little or no flash, and high dimensional stability. Fast cycle times, reduced mold wear, elimination of secondary operations, and other processing and performance gains of LCPs often lead to lower overall finished part costs even below those of less-expensive resins.

During injection mold filling, the fountain flow effect of LCPs causes surface molecules to stretch in the flow direction. These molecules ultimately form a highly oriented skin (15%–30% of a part's thickness) that is self-reinforcing. This results in exceptional flexural strength and modulus, as well as good tensile performance. For example, LCPs have a modulus from 1.4×10^6 to 3.5×10^6 lbf/in.² (10–24 GPa), a tensile strength from 18×10^3 to 37×10^3 lbf/in.² (124–255 MPa), and notched Izod impact values up to 7 ft-lb/in (374 J/m).

The LCPs retain 70% of their notched Izod impact values down to a temperature of about –270°C (–450°F). They are also resistant to bleaches, chlorinated organic solvents and alcohols. They have extremely low gas-permeation rates compared to commercial packaging films. Their ionic extractables are well below those needed for corrosion-free environments for integrated circuit chip applications. The

LCPs are also inherently flame retardant and possess a high LOI ($> 35\%$). Their combustion produces a low smoke density and relatively nontoxic products.

Because LCPs are thermoplastic and have excellent thermal stability, high levels of regrind can be used in injection molding of components. As a guide, 50% regrind is usually acceptable.

5.3.5 Applications

One of the first applications of LCPs was a range of dual-ovenable cookware of Xydar made by Tupperware, a subsidiary of Dartco Manufacturing. The resistance of LCPs to chemicals and solvents and good performance in hostile environments have led to their several specialized applications. Vectra materials have been used commercially for the molding of formic acid separation tower packings as they have proved to be more efficient and longer lasting than conventional ceramic packing materials.

LCPs are also used in such demanding areas as surgical instruments, aircraft and automotive engine systems, fiber optic devices, chemical equipment, and photocopier components.

LCPs are finding use as replacement for epoxy and phenolic resins in electrical and electronic components, printed circuit boards (PCBs), and fiber optics. In these applications, the high mechanical properties, low coefficient of thermal expansion, inherent inflammability, good barrier properties, and ease of processing of LCPs (Vectra in particular) are important.

In fiber optic applications, LCPs can be extruded into a variety of shapes and sizes using conventional extrusion equipment found in typical fiber optic wire and cable production plants.

Having one of the highest flow rates of any polymer and virtually no deformation or shrinkage on molding, LCPs are typically used for precision parts with thin walls and complex shapes. In the electronics industry, the benefits mentioned above—plus the resin's resistance to soldering temperatures of 200°C – 250°C —give it an edge over other high-performance plastics in many surface-mounted devices. For example, finely dimensioned electronic components such as SIMM socket with 0.050-in. spacing between pins are typical uses of LCPs.

In several electronic applications, such as connectors and capacitors, LCPs are also being used in preference to high-performance materials, such as PPS, because of their ease of processing, greater impact resistance, and overall lower part cost.

5.4 Electroactive Polymers

As computers and sophisticated electronics devices began to move out of their shielded rooms into offices, stores, and homes, it became highly desirable to take advantage of the light weight, low cost, and aesthetics that could be gained by substituting plastics for metal housings for the instruments [12–16]. Conductive plastics have therefore been increasingly used to provide flexible, lightweight, and moldable parts having good static bleed-off and electromagnetic interference (EMI) shielding properties. A variety of uses of such materials are encountered, ranging from compliant gasketing to rigid housing for business machines.

Conductive polymers fall into two distinct categories: filled polymers, which are used for a wide range of anti-static and static-discharging applications, and intrinsically conductive polymers, which contain no metals but conduct electricity when chemically modified with dopants.

A number of other polymeric solids have also been the subject of much interest because of their special properties, such as polymers with high photoconductive efficiencies, polymers having nonlinear optical properties, and polymers with piezoelectric, pyroelectric and ferroelectric properties. Many of these polymeric materials offer significant potential advantages over the traditional materials used for the same application, and in some cases applications not possible by other means have been achieved.

5.4.1 Filled Polymers

Polymers can be made to conduct electricity relatively easily by compounding them with high loadings of conductive materials as fillers. Apart from the inherent properties of the fillers, parameters such as

concentration, particle form (sphere, flake, fiber), size, distribution, and orientation are deciding factors that influence the properties of filled polymers.

When choosing a filler, the following requirements merit consideration: (1) the filler has high conductivity to avoid excess weight; (2) it does not impair the physical/mechanical properties of the plastic; (3) it is easily dispersed in the plastic; (4) it does not cause wear on forming tools (injection molding, extrusion); (5) it has favorable cost picture; and (6) it produces good surface structure of the finished product. The commonly used electrically conducting fillers are carbon, aluminum, and steel. The most common metallic conductor, copper, is not used because it oxidizes within the plastic and impairs its physical properties.

Typical dimensions for common fillers are:

Aluminum flakes: length 1–1.4 mm, thickness 25–40 μm

Carbon black: spherical, diameter 25–50 μm

Graphite fiber: length mm-cm, thickness 8 μm

Steel fiber: length 3–5 mm, diameter 2–22 μm

All of them are to be found in a number of qualities with varying prices and conduction properties.

Depending on particle form and orientation, there is a certain critical volume concentration at which the resistance decreases, i.e., the conductivity increases, drastically. This is shown in Figure 5.12. At the critical concentration, the filler can form a continuous phase through the matrix in the form of microscopic conductive channels. As shown in Figure 5.12, the specific resistance of filled polymers also depends on the inherent conductivity and particle form of the filler besides its concentration. The critical concentration can be reduced to low levels by using conductive particles that are fibrous in shape. The reduction in critical volume loading is proportional to the magnitude of the fiber's aspect ratio (length/diameter).

It has been shown that even extremely small concentrations of additives can make plastics conductive if they are in the form of conductive fibers with length to diameter (L/D) ratio of 100 or more. The striking difference between the use of chunky fragments and fibrous materials in their effect on conductivity can be seen from the diagram in Figure 5.13.

If one loads a plastic with 5 percent by volume of 6-mil size in a random distribution (Figure 5.13a), there will be, on the average, a 6-mil gap to the nearest sphere. Heat or electrons flowing through such a matrix would thus cross alternate paths of about equal lengths in the two media. The picture, however

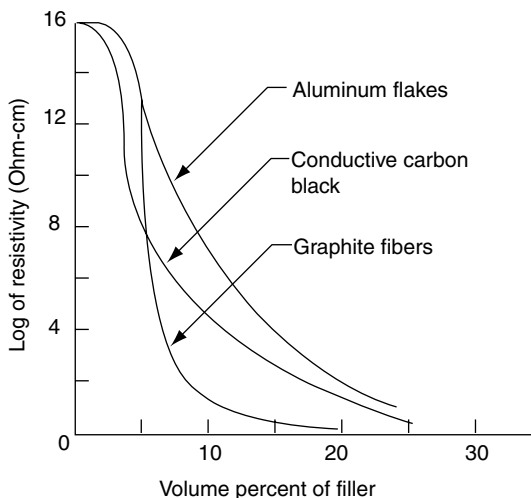


FIGURE 5.12 Composite resistivity as a function of filler volume loading and filler type.

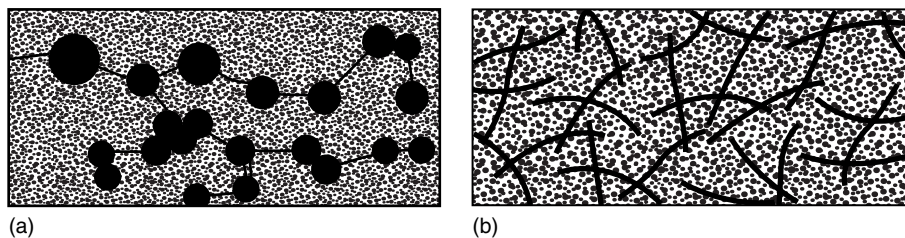


FIGURE 5.13 Comparison of typical flow path through composites using the same volume percentage of material as spheres and fibers ($L/D=100$). (a) Chunky particles—long path through plastic; (b) fibers—short gaps in plastic.

becomes quite different if the same 5 percent of material is dispersed as 1-mil diameter and 100-mil long fibers. It is inevitable that at random orientations they will touch one or more of their nearest neighbors, as shown in Figure 5.13b, thereby providing an almost continuous path through the composite along the conductive fibers. Fibers will therefore be more effective in lowering the electrical resistivity of plastic and increasing the thermal conductivity than chunky fragments.

The above concept led to the creation of metalloplastics—a family of conductive plastics in which the conductivity is great enough to make the material resemble metal both electrically and thermally. To serve as a practical engineering material, metalloplastics should have electrical resistivities of less than 1 ohm-cm and thermal conductivities of at least a factor of ten higher than those of normal plastics.

The importance of high thermal conductivity in plastics is being recognized as the automobile business tries hard to use more and more plastic parts to reduce the weight of the automobile. With conventional plastics having poor thermal conductivity, the problem of getting heat into the part to form it and then getting the heat out again results in cycle times of the order of minutes, not seconds. This implies an

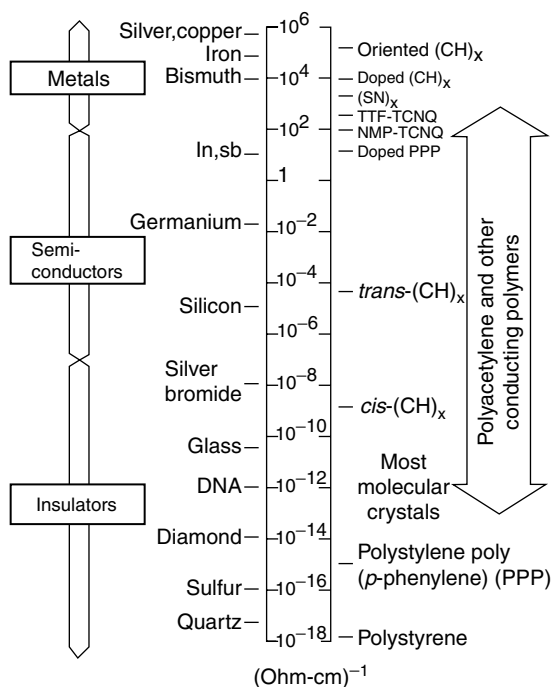


FIGURE 5.14 Chart of conductivities for selected materials. [Note: $1 (\text{ohm-cm})^{-1} = 1 \text{ S cm}^{-1}$.

increase of one to two orders of magnitude in the number of tools necessary to make the same number of parts. So, for the auto industry, an order of magnitude increase in thermal conductivity could be a very significant advance.

Metalloplastics with electrical resistivities as low as 0.01 ohm-cm and up to 100-fold higher thermal conductivity than ordinary plastics have been developed by the addition of a few percent of metal and/or metallized glass fibers (L/D of the order of 100/1) to plastics. Use of such materials can have very significant effects on molding cycle times, uniform heating and cooling rates, and heat transfer rates in the final product.

Whereas, thermal conductivity is proportional to the concentration of conductive fillers and is increased even by such low concentrations of the fibers that one fiber does not touch its neighbors, the electrical resistivity is not significantly modified until an almost continuous path is available through the conductive fibers. Plastics can thus be developed that are improved in thermal conductivity but can be used for electrical insulation or resistive heating. Suitably filled polymers are thus used to drain off heat in pressure switches as well as in polymeric tapes intended for self-regulating, resistive heating of water pipes, railroad switches, etc.

Filled conductive polymers are 10–12 orders of magnitude more conductive than unfilled polymers but are still several orders of magnitude lower than copper (Figure 5.14). Carbon-black filled polymers are the most common. Fillers other than carbon black include finely divided metal flakes and fibers, metallized glass fibers, and metallized inorganics such as mica.

Filled conductive polymers used for packaging include polycarbonate, polyolefin, and styrenics incorporating fillers such as carbon, aluminum, and steel flakes and fibers. A polycarbonate/ABS blend (Bayblend ME) introduced by Bayer is 4% aluminum filled and suited to many screening functions.

The electrically conductive polymers have their greatest use in EMI-shielded casings and protective housings of electronic and telecommunications equipment, where they have rapidly substituted metal because of their low weight and easy workability. Steel fiber is mostly used in filled conductive polymers intended for EMI-shielding applications, which will be discussed below.

Conductive rubber has been used in a number of applications. In most cases, silicone rubber is used because of its greater resistance to temperature, UV light, oxygen, corrosive gases, chemicals, and solvents as compared to organic rubber. Conductive rubber is used in tires to leak off static electricity. Ethylene-propylene conductive rubber is used as a covering in cables to reduce high voltage problems. In all these cases, carbon black is generally used as the filler, one reason being that it also acts as a reinforcing filler, increasing the strength and tear resistance of the product. In the electronics industry, conductive rubber finds use as a connector for liquid crystal displays in electronic digital watches.

5.4.1.1 EMI Shielding

EMI is the random, uncontrolled, broad-range frequency radiation emitted from many natural and man-made sources. The recent rapid growth in man-made sources such as computers, telecommunication, and other business machinery has led to the legislation in the United States and Europe covering the levels of electromagnetic radiation emitted by electronic devices. The EMI-shield on most computers and electronic digital equipment on the American market has to conform to Federal Communications Commission (FCC) standards within the frequency range 30–1000 MHz. Similar regulations exist in Germany and are being implemented in other countries.

Metal or carbon particles in plastic reflect and absorb electromagnetic radiation. When dimensioning a shielding material, the absorption of non-reflected radiation must be made sufficient. An electromagnetic wave is absorbed according to the following correlation [13]:

$$A = 3.34 \quad t \sigma \mu \sqrt{F} \quad (5.2)$$

where

A absorption expressed in decibels (dB)

t material thickness in one thousandths of an inch (mils)

- σ conductivity relative to copper
 μ relative magnetic permeability
 F frequency in MHz

Experimentally, EMI shielding is determined by the attenuation of a high frequency signal transmitted through the test sample. The attenuation or shielding effect α expressed in decibels is calculated from the equation

$$\alpha(\text{dB}) = 20 \log_{10}(E_b/E_a) \quad (5.3)$$

where E_b is the field intensity (V/m) without shielding and E_a is the field intensity (V/m) with shielding.

Data for some homogeneous metallic materials are given in Table 5.7. Aluminum and steel are the commonly used metallic fillers, and of these, steel provides the most effective EMI-shielding because of its high relative magnetic permeability.

Steel fibers give very good shielding properties at considerably low percentages. At only 1 percent of steel fiber in plastic, a shielding of 45–60 dB at 1 GHz is obtained. The conductivity of the filled plastic then is approximately 1 (ohm-cm)^{-1} . One great advantage of such low percentages permitted by steel fibers is that the other properties of the plastics are left almost unaffected.

In carbon, the conductivity varies from $10^{-2} \text{ (ohm-cm)}^{-1}$ for amorphous carbon to approximately $300 \text{ (ohm-cm)}^{-21}$ in the longitudinal direction for PAN-based high modulus carbon fibers. Apart from relatively low conductivity, carbon has the same magnetic permeability as aluminum, i.e., approximately 1. In order to obtain a given damping, carbon-based fillers have to be added in higher concentrations in comparison with metallic fillers such as steel. However, special carbon black grades with microporous structure and increased conductivity can now be found that allow the construction of a conductive network at relatively low concentrations.

Although a plastic with conductive fillers does not provide the same degree of shielding as metal, a great number of filled plastic materials have been introduced commercially, which in 1–3 mm thicknesses give shielding effects of 30–40 dB. As can be seen from the relationship given in Table 5.8 between shielding effect expressed in dB and in percent, respectively, these dB numbers correspond to 99.9%–99.99% damping of the interference signal, which is considered satisfactory.

There are a range of conductive polymers on the market that are based on metal fillers such as aluminum flake, brass fibers, stainless steel fibers, graphite-coated fibers, and metal-coated graphite fibers. However, the most cost effective conductive filler is carbon black. Mention should also be made of

TABLE 5.7 Conductivity, Permeability, and Absorption Characteristics of Major Metals

Metal	Relative ^a Conductivity	Relative ^a Permeability (100 kHz)	Absorption Loss (dB/mil)		
			100 Hz	10 kHz	1 MHz
Copper	1.00	1	0.03	0.33	3.33
Silver	1.05	1	0.03	0.34	3.40
Aluminum	0.61	1	0.03	0.26	2.60
Zinc	0.29	1	0.02	0.17	1.70
Brass	0.26	1	0.02	0.17	1.70
Nickel	0.20	1	0.01	0.15	1.49
Iron	0.17	1,000	0.44	4.36	43.60
Steel (SAE 1045)	0.10	1,000	0.33	3.32	33.20
Stainless steel	0.02	1,000	0.15	1.47	14.70
Mu-metal	0.03	80,000	1.63	16.30	163.00
Permalloy	0.03	80,000	1.63	16.30	163.00

^a Relative to copper.

TABLE 5.8 Shielding Effect Expressed in Decibels, Percentage of Leakage, and Classification of Shielding Effect

Shielding Effect (α) ^a , dB	EMI Leakage (%)	Value Judgement (technical)
0–10	10^2 – 10^1	Insignificant
10–30	10^1 – 10^{-1}	Minimal
30–60	10^{-1} – 10^{-4}	Average
60–90	10^{-4} – 10^{-7}	Above average
90–120	10^{-7} – 10^{-10}	Maximum (surpassing present technology)

^a Defined by Equation 5.3.

other more exclusive fillers, such as fiber glass with a metallized surface (aluminum) and silver-coated glass beads.

Where color is not critical, carbon black filled conductive polymers provide the most cost effective way of producing EMI shielding. A range of carbon black filled conductive polymers are produced by Cabot Plastics under the trade name Cabelec. One application is in telephone microcomponents.

In addition to being invariably black, another disadvantage of carbon-black-filled polymers is that they do not have the impact resistance of commonly used materials. One solution to these problems has been found by the use of sandwich molding. The process, originally developed by ICI in the 1960s, involves the production of a housing with an inner core of conductive plastics surrounded by an outer skin of conventional engineering plastic. The process thus gives the designer the full aesthetic freedom of design and also gives a good in-molded surface finish.

A system for sandwich molding developed by Aron Kasei uses fiber-reinforced ABS as the outer skin and a PLS conductor (see below) as the inner core. Applications include keyboard housings, printer housings, CRT enclosures, and medical equipment housings.

Conductor PLS, offered by Aron Kasei, is a range of brass or aluminum-filled thermoplastics such as ABS, polypropylene, PBT, and polycarbonate. Housing for personal computers made of PLS is claimed to cost less than housing made of plastics coated with conductive paint.

Ube Industries offer a brass fiber-filled nylon-6 that is reported to have excellent EMI-shielding properties, high resistance to abrasion, high conductivity, and easy malleability.

Mobay has introduced a 40% aluminum flake-filled, flame-retardant grade polycarbonate/ABS blend that is molded into internal cover configurations for EMI shielding.

LNP Corporation offers conductive plastics with fillers such as aluminum flakes, nickel-coated fibers, stainless steel fibers, and carbon fibers in a range of engineering polymers including nylon-6,6, polycarbonate, ABS, PPS, and PEEK. The company's 40% flake-filled polycarbonate is used for microprocessor covers in mainframe computers and nickel coated fiber-filled PEEK for avionic enclosures.

A 10% stainless steel fiber-filled ABS, produced by Mitech Incorporated under the tradename Magnex DC is used to shield electronic components in Xerox's Model 2100 laser printer. Mitech also produces a flame retardant stainless steel fiber-filled ABS for large interior covers.

Lacana Mining Company has developed nickel-coated mica fillers (Suzerite E. Micon) that can withstand compounding, extrusion, and injection molding with no special treatment. The coating is done by a hydrometallurgical process patented by Sheritt Gordon Company. Wilson-Fiberfil also offers nickel-coated mica that at 45% loadings in polyolefins provides 40 dB shielding and can be used for small-part moldings.

Wilson-Fiberfil offers 1% steel fiber-filled polycarbonate (Electrapil R-5147) for EMI-shielding, which has the advantage that the other properties of the plastic are left mostly unaffected during both tooling and use.

5.4.1.2 Conductive Coating

Some of the more commonly used methods to produce EMI shielding consist of coating the plastic with a conductive layer by post-molding or in-molding processes. The coating methods mostly used are conductive paints, zinc arc spraying, vacuum metallizing, electroplating, and foil application.

The simplest method of coating is the use of conventional coating systems such as brush coating or spray gun. Nickel, copper, silver, or graphite can be coated in this way onto vinyl polymers, acrylics, and polyurethane. This method is the least expensive but it suffers from the disadvantage that the resin has to be tailored to the substrate to avoid cracking.

Nickel coating is the most popular. A film thickness of 50–70 microns can achieve attenuation levels of 30–60 dB. An acrylic-based nickel coating, MDT1001, from Mitsubishi Rayon Company is claimed to be 100 times more effective as an EMI shield than normal carbon-based coating; it dries at room temperature and does not require multiple coatings.

For solvent-sensitive plastics where paint systems are unsuitable, zinc arc spraying is sometimes used. In this method, the metal is melted by an electric arc and sprayed as droplets by compressed air onto the part to be coated. Consequently, only materials with very high melting points can be used. The method gives a hard, dense coating of good conductivity, but it requires expensive equipment.

In vacuum metallizing, which also requires a major capital investment in equipment, a metallic film, usually aluminum, is deposited onto a plastic by condensation from vapor under high vacuum. By rotating parts during application, a controlled film thickness can be obtained producing high levels of attenuation with layers as thin as 4–6 microns.

Electroplating with copper, nickel, or chromium using conventional techniques provides good conductivity and durability. It, however, requires paint finishing. Electroless plating, which differs from electroplating in that no external source is required to initiate and control the process, has proved to be an effective EMI-shielding process for components that may be conductive in some areas and nonconductive in others, such as computer housing.

In a selective electroless plating, a conductive film of copper or nickel is deposited onto a specific part of the molding as opposed to overall plating by conventional techniques that require paint finishing. Attenuation levels of 50 dB can be obtained at layers of 1–3 microns.

In one electroless plating technique, which reportedly achieves attenuation levels of 70 dB in layers of 1–2 microns thick, the molded part is immersed in an aqueous solution of copper salt, reducing agent, and initiator to obtain copper deposition as the primary shielding layer. Nickel is then added to form an outer layer that provides corrosion resistance and improved impact strength.

In the process of metal coating by ion plating or cathode sputtering, which is claimed to produce better adhesion of metal to the substrate compared to vacuum metallizing, positively charged gas ions are discharged between two electrodes and bombarded onto a metal target. As a result, the metal vaporizes and condenses onto the molding. A major drawback of the process is the cost of ion-plating equipment.

A relatively new approach to EMI shielding is in-mold coating. In a process developed by Dai Nippon Toryo and Tokai Kogyo, tradenamed NTS, the mold surface is coated with a metallic material tradenamed Metrafilm by electrostatic spraying. The coating and compound then bond during injection producing excellent adhesion. Since the metallic powder is encapsulated in a resin and does not contain any solvents, the process can be used for resins that are sensitive to solvents such as polystyrene.

5.4.1.3 Signature Materials

Operative conditions of weapons carriers can be drastically influenced (stealth technology) by the so-called signature adaptation, which provides reduced probability of detection by radar, infrared, visual, or acoustical reconnaissance. The active materials are applied mostly as top layers, such as camouflage painting, radar layers, IR-layers, and acoustical damping layers, and are often used in combination. Thickness and material properties are adjusted to give minimal reflection against incident electromagnetic radiation. During radar reconnaissance, this radiation falls in the frequency range of 3–30 GHz. In other cases, it may be a question of damping the natural radiation from the weapons carrier in the IR range of 2–20 μm .

In order to obtain low radar reflection with very thin layers, the following correlations should be fulfilled:

$$\begin{aligned}\varepsilon' &= \mu' \\ \varepsilon &= \mu''\end{aligned}\tag{5.4}$$

where ε' and ε'' are, respectively, the real part and the imaginary part of the permittivity ε , which in alternating

fields is generalized to a complex quantity:

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad (5.5)$$

The imaginary part ε'' is a measure for the dielectric losses of the material. Similarly, μ' and μ'' are defined in relation to the permeability μ' and μ'' are defined in relation to the permeability μ :

$$\mu = \mu' - j\mu'' \quad (5.6)$$

The correlations (4) above, result in the layer having the same wave impedance as air (120π), i.e., there is no reflection from the outer surface. The radiation passing through the layer is reflected back by the metallic base. If the dielectric and magnetic losses, represented by ε'' and μ'' respectively, are large, the greater part of the radiation can be absorbed by the layer even if it is thin.

For several decades, efforts have been made to produce materials with these properties. Since the end of the sixties, great interest has been shown towards magnetic absorption materials based on ferrite powder dispersed in organic binder agents. Ferrite represents a group of ceramic materials with the principal formula $(M^{II}O)(F_2O_3)$, where M^{II} is a divalent metal, e.g., Fe, Co, Ni, Mn, Zn, or Cd.

The magnetic losses of the ferrite produce a high resonance peak at a certain frequency, above which they diminish linearly to the wavelength. The phenomenon can be used to obtain thin, absorbent, wide-band layers. No reflection occurs at the outer surface when the impedance at the surface air/ferrite becomes equal to in-impedance of the layer. The in-impedance is, in effect, a sum impedance because the greatest part of the incident radiation is reflected several times between the interfaces of the layer.

The development in the ferrite area is intensive and is aimed at increasing the medium-frequency in the GHz-range with preserved band-width. Much of the development in the area is covered in secrecy.

Mention should also be made of signature adaptation that makes use of negative interference to reduce the probability of detection. In this case, the signature protective layer is adjusted so that negative interference occurs between the radar radiation that is reflected respectively from the outer surface and from the underlying metal, thus causing a black-out of the net reflection from the surface. The reflections in this case need to be adjusted so that 50% is reflected at the outer layer and 50% at the metal surface and so that the phase shift between these reflected radiations becomes half a wavelength at the outer surface.

Interference layers in the form of filled polymers have been used on warships. A simple system is polyester filled with TiO_2 . It, however, provides protection only within a very narrow frequency range.

5.4.2 Inherently Conductive Polymers

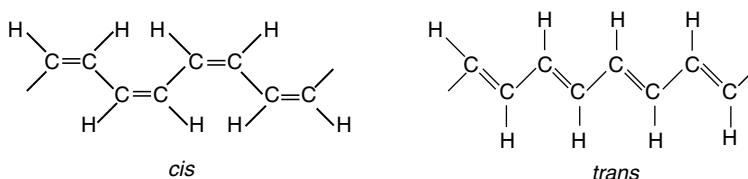
Interest in electrically conducting polymers began in the mid-1960s with the suggestion of Little [17] in his theoretical studies that some organic materials could become superconductors. The first example that has been extensively studied is tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) and its derivatives. The first covalent polymer exhibiting the electronic properties of a metal was polymeric sulfur nitride, $(SN)_x$, which attracted much attention in the mid- to late 1970s.

In 1977, the first covalent organic polymer, polyacetylene $(CH)_x$, that could be doped through the semiconducting to the metallic range, was reported. Another significant breakthrough occurred in 1980 with the discovery that PPP could be doped to conductivity levels quite comparable to those in polyacetylene. This polymer is the first example of non-acetylene hydrocarbon polymer that can be doped to give polymers with metallic properties.

Polyacetylene has been investigated much more extensively than any other conducting polymer and has served as a prototype for the synthesis and study of a large number of other conjugated, dopable organic polymers. Of these, the greatest research efforts are devoted to polypyrrole, PPS, PPP, polythiophene, and polyaniline.

In a nondoped state, the basic polymers have low conductivity (Figure 5.14). The two polyacetylene conformations *cis* and *trans* are in the semiconductor range; PPP is a good insulator.

The synthesis of the polyacetylene powder has been known since the late 1950s, when Natta used transition metal derivatives that have since become known as Ziegler–Natta catalysts. The characterization of this powder was difficult until Shirakawa and coworkers [18] succeeded in synthesizing lustrous, silvery, polycrystalline films of polyacetylene (which has become known as “Shirakawa” polyacetylene) and in developing techniques for controlling the content of *cis* and *trans* isomers:



Coordinative polymerization of acetylene using the Ziegler–Natta catalytic system, $\text{Ti}(\text{OBu})_4\text{-AlEt}_3$, is the most powerful way of forming polyacetylene powders, gels, or films. Polyacetylene films may be prepared by simply wetting the inside walls of a glass vessel with a toluene solution of AlEt_3 and $\text{Ti}(\text{OBu})_4$ and then immediately admitting acetylene gas at any pressure up to 1 atm. A cohesive film grows over a period of time with thickness varying from 10^{-5} to 0.5 cm, depending on the pressure of acetylene and the temperature used. The film is formed completely as a *cis* isomer if a polymerization temperature of -78°C is used and as the *trans* isomer if a temperature of 150°C is used (with decane solvent), while with room temperature polymerization, the film is approximately 60% *cis* and 40% *trans* isomer.

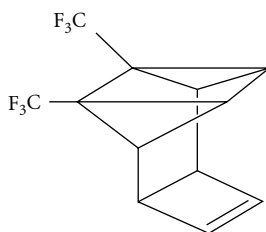
The *cis* isomer may be converted to the *trans* isomer, which is the thermodynamically stable form, by heating at 150°C for 30 min to 1 hr. The *cis*–*trans* content is conveniently determined from the relative intensities of bands in the IR spectra.

The morphology of all polyacetylenes made with various Ziegler–Natta catalysts is fibrillar. The conductivity of films of polyacetylene depends on the *cis*–*trans* content, varying from $10^{-5} (\text{ohm}\cdot\text{cm})^{-1}$ for the *trans* material to $10^{-9} (\text{ohm}\cdot\text{cm})^{-1}$ for the *cis* isomer. Doping increases the conductivity of both *cis*- and *trans*-polyacetylene drastically.

The polyacetylene made with the Ziegler–Natta catalytic system is infusible, insoluble, usually contaminated by catalyst residues, and tends to become brittle and dull when exposed to air due to slow oxidation. These features make it difficult to process or handle, and attempts have been made to either improve the polymer or make derivatives or precursors that are soluble in organic solvents.

Many of these problems have been solved by Feast and coworkers [19], who at the University of Durham developed a very elegant synthetic method, now commonly known as the Durham route. This is a two-stage process in which soluble precursor polymers are prepared by a metathesis ring-opening polymerization reaction and these are subsequently heated to produce polyacetylene by a thermal elimination reaction. An example of the method, given in Figure 5.15, involves the tricyclic monomer (A) which undergoes metathesis polymerization to precursor polymer (B). Thermal degradation of the latter yields *trans*-polyacetylene.

A refinement of the process in Figure 5.15 involves photochemical conversion of (A) with $\text{R} = \text{CF}_3$ into



which on polymerization produces a precursor that is stable at room temperature and is converted to *trans*-polyacetylene on heating at 57°C – 67°C .

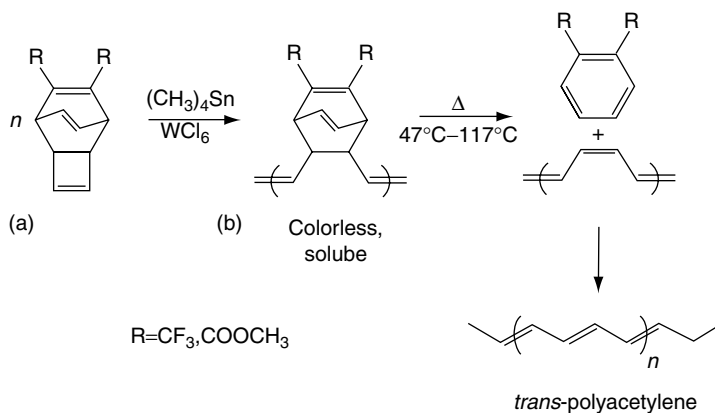
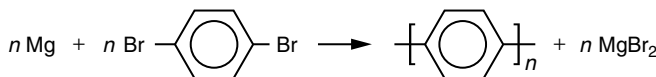


FIGURE 5.15 Durham route for the synthesis of polyacetylene.

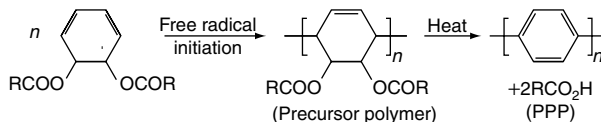
The advantages of the Durham route are: (1) contaminating catalyst residues can be removed because the precursor polymers are soluble and can be purified by dissolution and reprecipitation; and (2) the precursors can be cast as films or drawn and oriented prior to conversion to the all-*trans* form of polyacetylene. This allows a degree of control over the morphology of the final product which in the pristine state appears to be fibrous and disordered. Because conductivity increases by alignment of the polymer chains, stretching the film or fiber assists this process and this can be performed using the prepolymer.

The PPP structure has all the characteristics required of a potential polymeric conductor, but it has proved difficult to synthesize a high-molecular-weight material. One method is the polycondensation



but this only yields oligomeric material, and even this is insoluble.

A novel route developed by workers at ICI overcomes these problems by again making use of a tractable intermediate polymer. Thus radical polymerization of an ester of 5,6-dihydroxycyclohexa-1,3-diene leads to a soluble precursor polymer that can be processed prior to the final thermal conversion into PPP:



The polymer is very stable and can withstand temperatures up to 450°C in air without degrading. It is an insulator in the pure state but can be both *n*- and *p*-doped using methods similar to those for polyacetylene. However, as PPP has a higher ionization potential it is more stable to oxidation and requires strong *p*-dopants. It responds well to AsF_5 , with which it can achieve conductivity levels of $10^2 \text{ (ohm-cm)}^{-1}$.

5.4.2.1 Doping

Because electron mobility is almost nonexistent in most organic polymers, a mechanism for the creation of that mobility is needed and is generally accomplished by the doping process (oxidizing or reducing). In practice, doping occurs by exposing the polymer, most often in the form of thin film or powder, to the doping agent in gas phase or in liquid phase. The doping can also be done electrochemically by using the polymer as an electrode. The principal methods of doping are as follows [16,20].

1. Chemical doping. The doping is accomplished by exposing the polymer to the vapor of a dopant such as I_2 , AsF_3 , or H_2SO_4 , or by immersing the polymer films in a dopant solution, such as

sodium naphthalide in tetrahydrofuran, I_2 in hexane, and so on. The amount of dopant incorporated in the material (doping level) depends on the vapor pressure of the dopant or its concentration, the doping time, and the temperature.

2. **Electrochemical doping.** Polymers can be doped electronically in an electrochemical cell, such as by immersing the material as an electrode in an organic electrolyte solution ($LiClO_4$ in tetrahydrofuran or propylene carbonate, with lithium as a counter electrode) or in aqueous electrolytes ($PbSO_4/PbO_2$ in sulfuric acid solutions, with lead as a counter electrode).

Figure 5.16 shows, schematically, electrochemical doping in comparison with chemical doping. During electrochemical doping, the electrons are driven by an outside source of current. The lack of electrons and then the surplus of electrons which occurs, is balanced electrostatically by the dissociated ions in the electrolyte, which diffuse into the polymer. The end result is a polymer that is *p*-doped and *n*-doped, respectively.

3. **Ion implantation.** Polymers, when exposed to proper ion beams, can become conducting due to the implantation of ions in the polymer's lattice, which form covalent bonds with the material. The doping level depends on the energy of the ion beam.
4. **Photochemical doping.** This is accomplished by treating the polymer with a dopant species that is initially inert towards the materials, followed by irradiation. For example, diphenyliodonium hexafluoride arsenate in methylene chloride or triarylsulfonium salts, followed by ultraviolet irradiation.

The academic research in the area of conductive polymers was mainly directed towards polyacetylene, while industry, gave priority to more stable basic materials such as PPP, polypyrrole, PPS, and

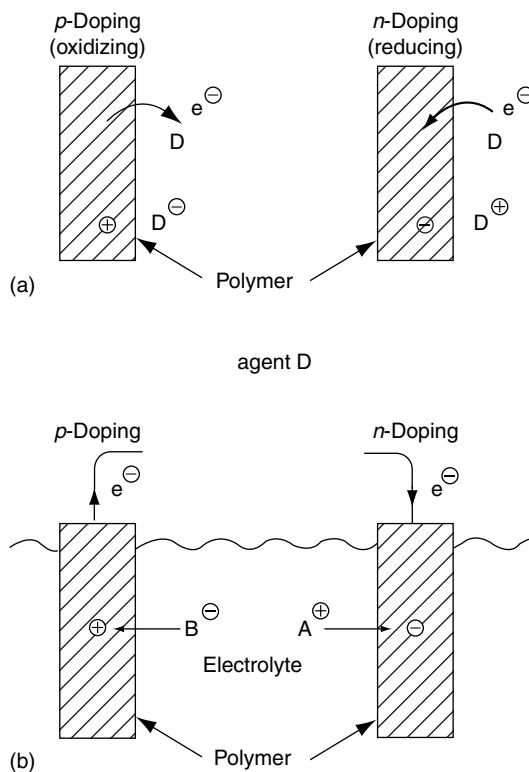


FIGURE 5.16 Schematic comparison of chemical doping and electrochemical doping. For electrochemical doping an outside power source is required (not drawn). (a) Direct charge transfer with doping agent D in chemical doping. (b) Charge transfer in electrochemical doping.

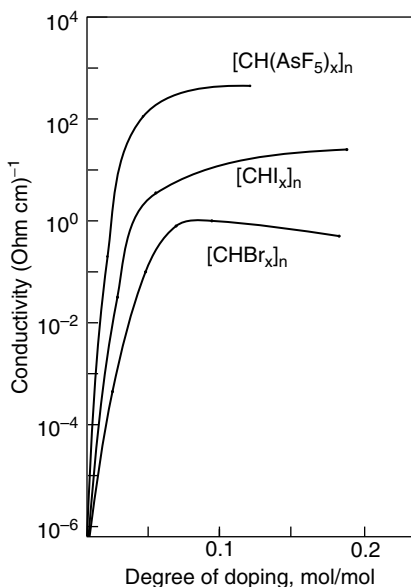


FIGURE 5.17 Variation of conductivity of polyacetylene on degree of doping. (After Chiang, C. K., Gau, S. C., Fincher, Jr., C. R., Park, Y. W., Macdiarmid, A. G., and Heeger, A. J. 1978. *Appl. Phys. Lett.*, 33(1), 18.)

polythiophene. Today, the academic research is extensive even in those areas, as well as a number of other conjugating polymers. A large number of dopants have been used to dope polyacetylene and other conjugated polymers.

Electron-attracting dopants, such as Br_2 , I_2 , AsF_5 , H_2SO_4 and HClO_4 may oxidize polyacetylene to produce *p*-type conductivity. As shown in Figure 5.17, the conductivity increases continuously with the degree of doping to a saturation level. Some of the powerful dopants have been used to oxidize other conjugated polymers. Some examples of *p*-type dopants and their measured room temperature conductivities are given in Table 5.9.

Electron-donating dopants may reduce polyacetylene or other conjugated polymers giving rise to *n*-type conductivity. Doping occurs when the polymer is immersed in a tetrahydrofuran solution of radical anion/alkalide where the alkalide components can be Li, Na, K, Cs, or Rb, and the radical anion can be naphthalene, anthracene, or benzophenone. A doping reaction such as the following occurs (Nph = naphthalene):



When the polymer is allowed to contact a K/Na alloy at room temperature, *n*-doping also occurs. In *n*-doped polymers, the polymer chain is considered as a polycarbanion associated with the corresponding M^+ metal ion. A few examples are given in Table 5.10.

Polyacetylene, because it represents the simplest of the conjugated organic polymers, has received much attention as a fundamental material, although other polymers such as polyphenylene, polypyrrole,

TABLE 5.9 Examples of Oxidation/*p*-Type Doping [16]

Doped Polymer	Conductivity, (ohm-cm) ⁻¹
$[\text{CH}(\text{I}_3)_{0.10}]_n^a$	5.5×10^2
$[\text{CH}(\text{AsF}_5)_{0.10}]_n^a$	1.2×10^3
$[\text{CH}(\text{SbF}_5)_{0.006}]_n^a$	5.0×10^1
$[\text{CH}(\text{H}_3\text{O}^+\text{HSO}_4^-)_{0.10}]_n^a$	1.2×10^3
$[\text{CH}(\text{FeCl}_3)_{0.09}]_n^a$	8.5×10^2
$[\text{CH}(\text{MoCl}_5)_{0.10}]_n^a$	2.0×10^2
$[\text{CH}(\text{ClO}_4)_{0.065}]_n^b$	5.0×10^2
$[\text{C}_6\text{H}_4(\text{AsF}_5)_{0.26}]_n^a$	1.5×10^2
$[\text{C}_6\text{H}_4\text{S}(\text{AsF}_5)_x]_n^a$	2.5×10^1
Polypyrrole/(C_6H_5) ₂ IAsF ₆ ^c	3.0×10^{-3}
Polyaniline/60% protonation	5.0×10^0

Note: 1 (ohm-cm)⁻¹ = 1 S cm⁻¹.

^a Chemical doping.

^b Electrochemical doping.

^c Photochemical doping.

TABLE 5.10 Examples of Reduction/*n*-Type Doping [16]

Doped Polymer	Conductivity, (ohm-cm) ⁻¹
[Li _{0.30} (CH)] _n ^a	2.0 × 10 ²
Na _{0.21} (CH)] _n ^a	2.5 × 10 ¹
[K _{0.16} (CH)] _n ^a	5.0 × 10 ¹
[(<i>n</i> -Bu ₄ N) _{0.03} (CH)] _n ^b	2.5 × 10 ¹
Polyquinoline/Li ^b	2.0 × 10 ¹
Polyquinoline/Na ^a	5.6 × 10 ⁻¹
(CH) _n /LiAlH ₄ ^a	6.0 × 10 ⁰

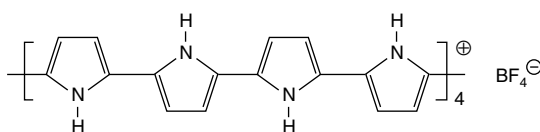
^a Chemical doping.^b Electrochemical doping.

polyquinoline, polyquinoxylene, polyphenylene sulfide, and polythiophene are also being increasingly studied. PPP was the first example of a nonacetylene hydrocarbon polymer having an intrinsic conductivity of less than 10⁻¹⁴ (ohm-cm)⁻¹, but, as with polyacetylene, PPP can be doped with AsF₅ to give conductivities of around 10² (ohm-cm)⁻¹. It may also be doped with alkali metals to provide highly conductive *n*-type materials.

The main advantage of poly-*p*-phenylene is that, due to its nonacetylenic composition, it has a much higher thermal stability (450°C in air and 550°C in inert atmosphere). Potential applications of poly-*p*-phenylene are similar to those envisaged for polyacetylene, such as Schottky barriers in photocells. (A Schottky barrier is a metal semiconductor contact that has rectifying characteristics similar to a *p-n* junction.)

One of the most scientifically and technologically studied organic polymers is polypyrrole. Polypyrroles (PPys) have prompted considerable research because they are the only conducting polymers that can be produced directly in the doped state. The highly stable, flexible films of polypyrrole produced by one-step electro-oxidation have room temperature *p*-type conductivities ranging from 10 to 100 (ohm-cm)⁻¹. No additional dopants are required to produce electrical conductivity.

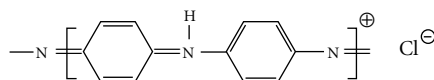
Typically, when a solution of pyrrole (0.06 M) and tetraethylammonium tetrafluoroborate Et₄N⁺BF₄⁻ (0.1 M) in acetonitrile containing 1% water is electrolyzed, an insoluble blue-black film of conducting polymer is produced at the anode. The film contains BF₄⁻, has a conductivity of about 100 (ohm-cm)⁻¹, and the composition is:



In addition to showing high electrical conductivity, polypyrrole films can be repeatedly electrochemically driven or switched between the blue-black conducting (100 ohm⁻¹ cm⁻¹) oxidized form and a yellow nonconducting neutral. The switching rate for thin films is approximately 1 per second.

One of the principal advantages of polypyrrole over other doped polymers is its excellent thermal stability in air. It is thermally stable up to 250°C, showing little degradation of its conducting properties below this temperature. Above 250°C, the rate of weight loss increases with temperature.

Polyaniline results from the reaction of aniline with ammonium persulfate in aqueous HCl. The reaction produces polyaniline as a dark blue powder with a conductivity of 5 (ohm-cm)⁻¹. The structure of the conducting form of the polymer is believed to be the di-iminium salt:



Polyanilines, from an industrial point of view, are in many applications the preferred conducting polymer system, as they offer a number of advantages over other conducting polymers. They are generally

soluble and environmentally stable polymers that are made by a one-step synthesis involving inexpensive raw materials. They offer extensive chemical versatility, which allows the properties of the polymer to be tuned to the needs of different applications. Thus, many polyaniline derivatives exist today as a result of chemical modification of polymer backbone, dopant, and oxidation state.

A number of water-soluble polyaniline derivatives have been developed in recent years. Incorporation of sulfonate groups onto the polymer backbone imparts water solubility to the polymer. In one process, this is accomplished by treating the polymer with fuming sulfuric acid which results in a sulfonic acid ring-substituted derivative that is alkali soluble but only upon conversion to the nonconducting sulfonate salt form.

A second method of introducing sulfonate groups is accomplished by deprotonating polyaniline base and reacting with a sultone, i.e., 1,3-propanesultone [22]. This gives rise to an *N*-substituted polyaniline derivative that is water soluble. Another route involves the polymerization of sulfonated aniline monomer such as sodium salt of diphenylaminesulfonic acid [23].

IBM has introduced a family of water-soluble polyanilines under the trademark PanAquas [24]. This is a series of polymers that are highly soluble in neutral water in the conducting form. They are made in a one-step straightforward synthesis involving a template-guided polymerization (Figure 5.18). In this process, the aniline monomer is first complexed to a polymeric acid and then polymerized in a controlled fashion to allow the polyaniline chain, as it grows, to wrap around the polyacid chain. The resulting polyaniline/polyacid blend is water soluble and is conducting. Different polyaniline derivatives can be made by this method by variations in the nature of the aniline monomer (i.e., variation in R in Figure 5.18) and in the nature of the polyacid. The conductivity of these polymers is on the order of 10^{-2} – 10^{-3} (ohm-cm) $^{-1}$.

PPS is unique amongst polymers utilized for electrical conduction in that it is available commercially as an engineering thermoplastic (Ryton by Philips Petroleum) and is finding use as a molding component for the encapsulation of electronic components.

Unfilled PPS is a white polymer with a melting point of 288°C and is intrinsically insulating, having a conductivity of less than 10^{-16} (ohm-cm) $^{-1}$. Doping with AsF₅ leads to an increase in conductivity to around 1–10 (ohm-cm) $^{-1}$, although there is also a deterioration in mechanical properties and a color change to dark blue.

Liquid-phase doping has been used for PPS. Thus, PPS has been doped and dissolved simultaneously by exposing PPS particles suspended in AsF₃ to the doping agent AsF₅. Films of doped PPS with good mechanical properties and conductivities up to 200 (ohm-cm) $^{-1}$ can be cast from such solutions of

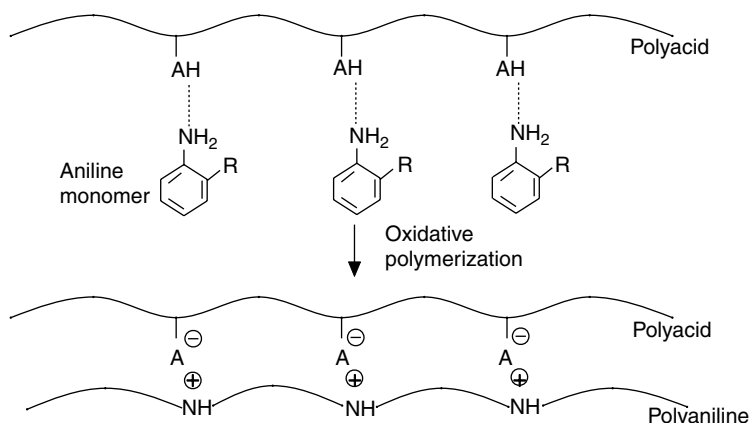


FIGURE 5.18 Template-guided polymerization to make water-soluble polyaniline (PanAquas). Aniline monomer is complexed to a polyacid template and then oxidatively polymerized in a controlled fashion. (After Nguyen, M. T., Kasai, P., Miller, J. L., and Diaz, A. F. 1994. *Macromolecules*, 27, 3625.)

AsF₅-doped PPS in AsF₃. The resulting films show improved strength and flexibility compared to those obtained by standard doping of solid PPS with AsF₅.

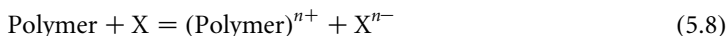
5.4.2.2 Conducting Mechanisms

The nature of the processes that induce high conductivity in polymers is different from those in the inorganic semiconductors. In the doping of inorganic semiconductors such as silicon, the dopant species occupies positions within the lattice of the host material, resulting in the formation of either electron-rich or electron-deficient sites with no charge transfer occurring between the sites. The doping reaction in polymers, on the other hand, is a charge-transfer reaction, resulting in the partial oxidation or reduction of the polymer, rather than the creation of holes.

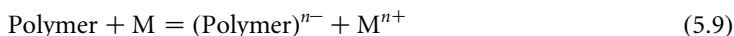
It is now well established [25] that the exposure of polyacetylene to an oxidizing agent X (or reducing agent M) leads to the formation of a positively (or negatively) charged polymeric complex and of a counterion which is the reduced X[−] (or the oxidized M⁺) form of the oxidant (or the reductant). Thus studies based on Raman spectroscopy and Mössbauer spectroscopy show that after exposure to iodine, the polyacetylene chain acts as a positively charged polycation with I₃[−] or I₅[−] acting as counterions.

Similar studies based on optical absorption and ESR spectra indicate that the reduction of polyacetylene by exposure to sodium naphthalide in tetrahydrofuran results in negatively charged (CH)_x[−] carbanions and N⁺ counterions.

The doping process in the case of conducting polymers may therefore be more correctly classified as redox processes of the following general scheme:



where X = I₂, Br₂, AsF₅, ..., in the case of an oxidation (*p*-doping) process and



where M = Na, Li, ... for a reduction (*n*-doping) process.

The above reactions are most likely to occur in the case of unsaturated polymers with π electrons as they can be easily removed from the polymeric chains to form polycations or added to the chains to form polyanions and, therefore, these are the types of polymers which assume high conductivity on doping.

Contrary to inorganic crystalline semiconductors, where charge is transported in general by electrons in the conduction band and holes in the valence band, in doped conjugated polymers charged solitons, polarons, and bipolarons act as charge carriers. These quasi-particles are the direct consequence of the strong electron-phonon interaction present in these quasi-one-dimensional polymers.

In polyacetylene, the *trans* structure is unique in that it has a twofold degenerate ground state as shown by sections (a) and (b) in Figure 5.19, which are mirror images, and the single and double bonds can be interchanged without changing the energy. Where an A sequence meets a B sequence, a free radical is produced (Figure 5.19c). This is a relatively stable entity and the resulting defect in the chain is called a neutral soliton (from solitary wave solutions, a mathematical treatment of conductivity), which corresponds, in simple terms, to a break in the pattern of bond alternation, i.e., it separates the

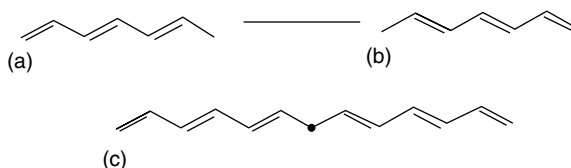


FIGURE 5.19 (a) and (b) Degenerate ground state of *trans*-polyacetylene. (c) Polyacetylene chain with a defect (neutral soliton).

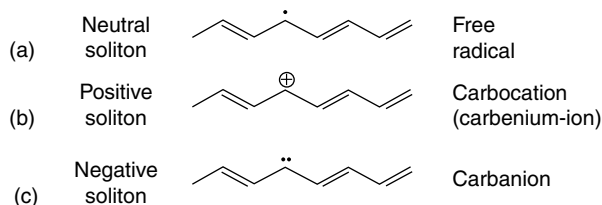


FIGURE 5.20 Formation from (a) a neutral soliton, (b) a positive soliton and (c) a negative soliton by controlled addition of *p*- and *n*-doping agents, respectively.

degenerate ground state structures. The electron has an unpaired spin and is located in a nonbonding state in the energy gap, midway between the two bands. It is the presence of these neutral solitons that gives *trans* polyacetylene the characteristics of a semiconductor with an intrinsic conductivity of 10^{-7} – 10^{-8} (ohm-cm) $^{-1}$.

This conductivity can be magnified by doping. Controlled addition of an acceptor or *p*-doping agent such as AsF₅, Br₂, I₂, or HClO₄ removes an electron and creates a positive soliton. In chemical terms this is the same as forming a carbenium ion (Figure 5.20b) that is stabilized by having the charge spread over several monomer units. Similarly, a negative soliton (Figure 5.20c) can be formed by treating the polymer with a donor or *n*-doping agent that adds an electron to the mid-gap energy level.

At high doping levels, the soliton regions tend to overlap and create new mid-gap energy bands that may merge with the valence and conduction bands, allowing freedom for extensive electron flow and thus making the polymer a conductor.

In the case of defect-free *trans*-polyacetylene chain, a charge transfer directly between doping agents and valence and conduction band, respectively, will produce an ion radical in the chain, i.e., a defect pair instead of an isolated defect. Figure 5.21 shows the mechanism of *p*-doping of *trans*-polyacetylene.

It can be shown theoretically that a separation of ion-radical components along the chain into one charged and one neutral soliton corresponds to a higher energy state compared to when the defect pair is held together. This more stable ion-radical pair is called polaron, and its formation is accompanied by two energy levels obtained symmetrically above and below the middle level of the band gap. When the doping degree is increased further, i.e., when polaron concentration is increased, the polarons begin to interact with each other. Two polarons interact to give two charged solitons (i.e., two unpaired electrons are united leaving behind two charged solitons), which produce a band halfway between the valence band and the conduction band.

A lattice of charged solitons (Figure 5.21) is obtained at about 4 mol% doping. At metallic conductivity, the soliton band overlaps the entire band gap between the valence band and the conduction band so that unpaired electrons with spin can contribute to the conductivity. This occurs at 11% doping of *trans*-polyacetylene.

In contrast to *trans*-polyacetylene, all other conjugated polymers, including *cis*-polyacetylene, possess nondegenerate ground states and this affects the nature of charge carriers they can support. In such

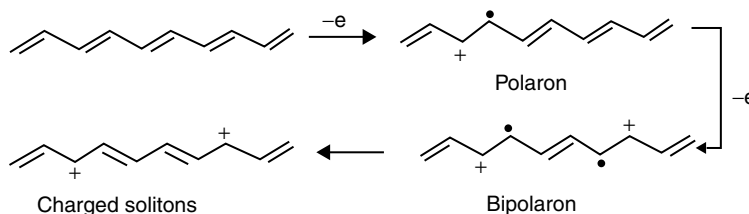


FIGURE 5.21 *p*-Doping of defect-free *trans*-polyacetylene.

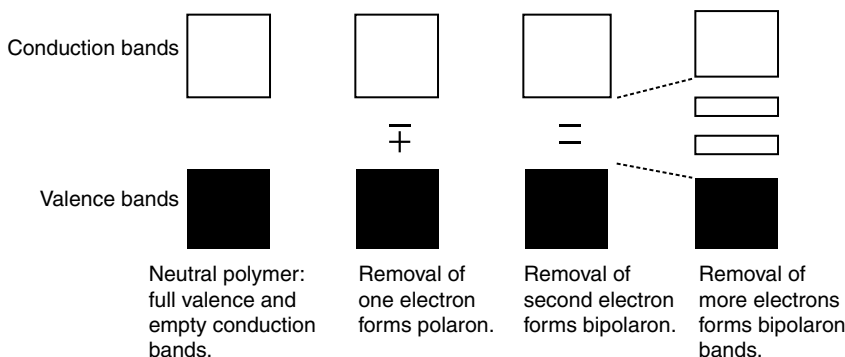


FIGURE 5.22 Band structure of the *p*-doped poly(*p*-phenylene).

polymers, it has been found that the formation of single solitons, whether as a result of doping or from inherent defects, is energetically unfavorable and the energetically preferred configurations involve paired sites. This can be illustrated by considering the example of PPP.

In PPP and most other polyconjugated conducting polymers, the conduction occurs via the polaron or bipolaron. The band structure for the *p*-doped PPP is shown schematically in Figure 5.22.

5.4.2.3 Applications

The interest on the part of industry in inherently conductive polymers is great because of the possibilities that lie in the workable qualities and light weights of polymer materials. The principal interest is, however, in their potential use for rapid, low-cost processing using film-forming polymer solutions.

5.4.2.3.1 Rechargeable Batteries

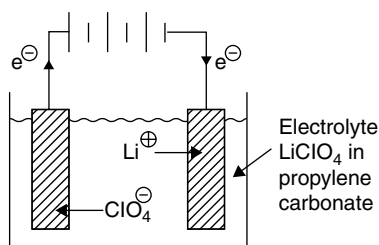
One of the most promising areas of application of inherently conducting polymers is as electrode materials in rechargeable batteries. Conducting polymers are promising charge storage materials because of their high charge carrier concentrations.

A polymeric electrode is doped electrochemically when the battery is charged, and is undoped at discharge (see Figure 5.16). The fundamentally appealing aspect of polymer electrodes is that charge and discharge are based on purely physical and reversible processes. There are no chemical processes to consume material. Whereas metal electrodes are continuously subjected to dissolution and redeposition during the charge-discharge cycles, resulting in mechanical wear, with polymer electrodes the ions can enter or leave without significant disturbance of the polymer structure. Polymer electrodes thus have a longer life than metal electrodes.

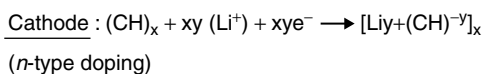
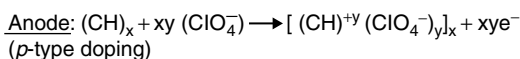
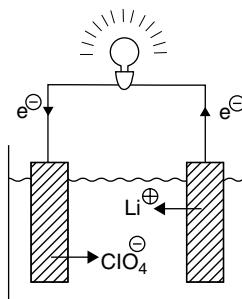
A battery cell where both the electrodes consist of dopable polymer is shown in Figure 5.23. The electrolyte in this case consists of $\text{Li}^+\text{ClO}_4^-$ dissolved in an inert organic solvent, usually tetrahydrofuran or propylene carbonate. When two sheets of polyacetylene or PPP are separated by an insulating film of polycarbonate saturated in an electrolyte (lithium perchlorate), and completely encapsulated in a plastic casing, a plastic battery can be made. The two sheets of polyacetylene or PPP act as both anode and cathode for the battery. A schematic is shown in Figure 5.24. Although doped polyacetylene and polyaniline electrodes have been developed, polypyrrole-salt films are the most promising for practical application.

It is also possible for only one electrode to consist of dopable polymer and for the other be of metal, usually lithium (Figure 5.25), which is preferred because of its low weight and high thermodynamic electrode potential.

The comparable data for two conventional and two polymeric batteries, which are given in Table 5.11, show that, in energy absorption per unit weight, the polymeric batteries are not superior to the lead-acid battery. What is most significant, however, is the fact that the power density is calculated here to be higher

Charge

Electrode reactions at charge:

Discharge

Electrode reactions at discharge are as above but in reverse.

FIGURE 5.23 Secondary battery with Pac electrodes. Here Pac is given the chemical symbol $(\text{CH})_x$.

by an order of magnitude. This reflects, apart from the higher voltage, the considerably higher current density in polymer batteries that is attributed to the fact that the ions in the electrolyte are able to wander quickly in and out in the electrode as it is doped and undoped. This is facilitated by the porous nature of polyacetylene film consisting of very thin fibers with a diameter of about 200 Å (2×10^{-8} m), which only

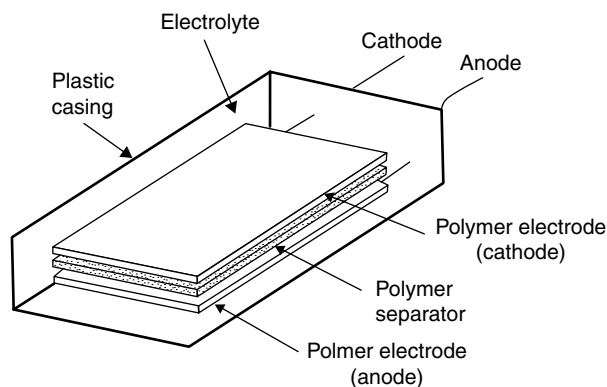


FIGURE 5.24 Schematic of plastic battery.

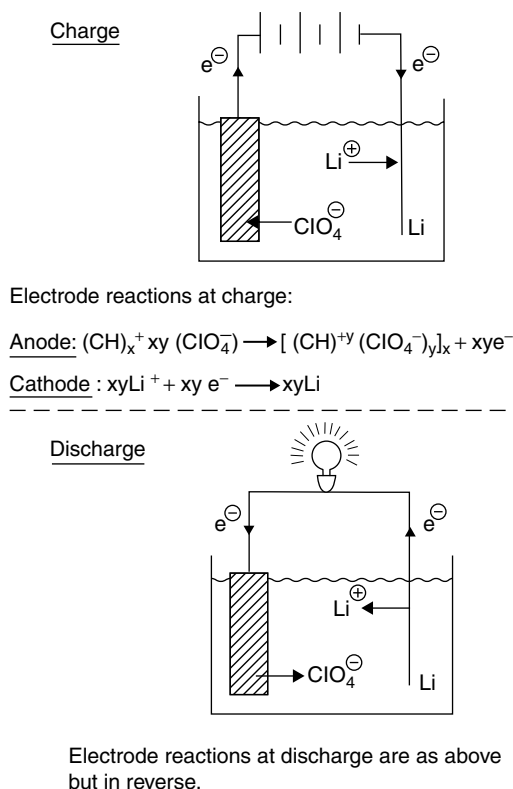


FIGURE 5.25 Electrochemical oxidation and reduction reactions in polyacetylene/lithium batteries.

the invention that would make electric cars a reality, because the lightweight polymer batteries would not weigh a car down to the extent as the heavy lead acid batteries would do.

An all-plastic battery may have many advantages [26]. For example, a car battery made of polyacetylene could weigh only one-tenth of that of a conventional lead-acid battery. Moreover, batteries with plastic electrodes could be fabricated into odd shapes, such as a flat disc that could be slotted into a car door. Prototype batteries have been made using polyacetylene and poly-*p*-phenylene electrodes, but a number of technical problems, such as long-term mechanical integrity need to be solved.

A derivative of polyacetylene that is more stable in air and soluble in organic solvents when doped with iodine, is polytrimethyl-silylacetylene (PTMSA). Though the derivative has a conductivity only one ten-millionth that of doped polyacetylene, it can be used as precursor to a wide range of other conductive derivatives. One such derivative is polyfluoroacetylene (polyacetylene in which all of the hydrogen atoms are replaced by fluorine), which according to calculations, would be electrically conductive without the need of dopants.

occupies one-third of the volume of the film and gives the material an exceptionally large effective surface ($40\text{--}50 \text{ m}^2/\text{g}$).

Though the rate of diffusion for a doping agent in polyacetylene itself is very low ($D = 10^{-15} \text{ cm}^2/\text{s}$ for Li in polyacetylene), it is compensated for by the fiber structure, which reduces the diffusion length when the material is impregnated with a liquid electrolyte.

Though the charging and discharging of polymer electrodes are based on purely physical and reversible processes, in practice, however, disturbing side reactions occur that give reduced efficiency. This happens especially at complete discharge-recharge. Therefore, only about one-third of the total charge should be utilized. (However, this also applies to lead-acid batteries where the normal operating range is between 40% and 80% of full charge.) Better cell construction and more stable electrolytes need to be developed in order to increase efficiency and useful life of polymeric batteries.

In order for electrically operated vehicles to become generally accepted, batteries with higher energy- and power-density in combination with lower weight and volume are required. Polymeric batteries show promise of making this a reality. Indeed, polymer batteries have been heralded as

TABLE 5.11 Comparison of Conventional and Polymeric Batteries [13]

Battery Type	Initial Voltage (V)	Energy Density (Wh/kg)	Power Density (kW/kg)
Lead-acid battery	2	30	0.4
Zinc-bromine	1.8	65	0.14
$(\text{CH})_x/(\text{CH})_x^a$	3.7	30	5
$(\text{C}_6\text{H}_4)_x/(\text{C}_6\text{H}_4)_x^b$	4.4	40	5

^a Polyacetylene electrodes.

^b Poly(*p*-phenylene) electrodes.

The Bridgestone Corporation of Japan has developed coin-type rechargeable polymer lithium batteries with a conducting polymer polyaniline and the high capacity lithium aluminum alloy as the two electrodes. The characteristics of these batteries are low self-discharge, high voltage, and long-term reliability. One of the unique features of this rechargeable polymer lithium battery is that it can be used as a power source in combination with solar cells. This feature opens up significant possibilities for application as a power source. The operation of electronic clocks, watches, calculators, remote control devices of audiovisual units, etc., are some of the potential application areas of this technology.

5.4.2.3.2 Electrochromic Devices

An electrochromic display (ECD) is a thin solid state device that changes color reversibly when subjected to a small electrical potential. Since the doping processes of certain conducting polymers are accompanied by changes in the color, this effect has been conveniently exploited in the realization of ECD devices. Thin films of a conducting polymer polythiophene, for example, are red in the doped state and deep blue in the undoped state.

The fact that a material changes color is, however, not sufficient to permit its use in a display system; its switching time between these two states must be very short and it should maintain these properties over many doping/undoping cycles. In the case of polythiophene, switching time of around 30 millisecon and a stability exceeding one million doping/undoping cycles have been measured. These values correspond to about 2 years of operation for a frequency of one cycle per minute.

Some of the applications of ECDs include time tables in airports and train stations, calculators, computers, clocks, and any other piece of equipment that utilizes a liquid crystal display.

ECD devices have several advantages over liquid crystal devices. ECDs have low power consumption, good optical contrast, a wide viewing angle, and an all solid-state construction. ECD devices may be constructed in large dimensions and have optical memory since the color acquired remains also after the driving voltage has been removed.

The disadvantage of an ECD is mainly associated with its comparatively slow response time since the driving mechanism deals with ions which generally have low diffusion coefficients in polymers.

The principle of electrochromic devices can be exploited in tinting ordinary window glass. Very thin polymer layers embedded in a colorless solid electrolyte and sandwiched between two layers of glass may tint a window when an electric potential is applied. The degree of tinting can be controlled by the size of the electric potential.

5.4.2.3.3 Sensors

Because their chemical and physical properties may be tailored over a wide range of characteristics, the use of polymers is finding a permanent place in sophisticated electronic measuring devices such as chemical sensors, pH sensors, ion-selective sensors, humidity sensors, biosensor devices, etc [27]. Chemical sensors are used for detecting and measuring the concentration of various chemical species in liquid or gas phase. The conductivity of conducting polymers with conjugated π bonds depends on the electronic structure, which can undergo changes under the influence of chemical species adsorbed on the surface. For example, such changes may result from redox or acid-base type interactions between polymer and the chemical species.

Conducting polymer sensor arrays for gas and odor sensing based on substituted polymers of pyrrole, thiophene, aniline, indole and others were reported in 1984 at the European Chemoreception Congress (ECRO), Lyon, followed by a detailed paper in 1985 [28]. Nucleophilic gases (ammonia and alcohol, such as methanol and ethanol, vapors) cause a decrease in conductivity, while electrophilic gases (NO_x , PCl_3 , SO_2) have the opposite effect. Most of the widely studied conducting polymers in gas sensing applications are polythiophene and its derivatives [29], polypyrroles [30], polyaniline and their composites [31,32].

Electrically conducting polystyrene/polythiophene, polystyrene/polypyrrole, polyacrylonitrile/polypyrrole, polycarbonate/polythiophene, polycarbonate/polypyrrole composites are prepared by

electropolymerization of the conducting polymers into the matrix of the insulating polymers polystyrene, polyacrylonitrile, and polycarbonate, respectively.

Acrylic acid doped polyaniline exhibits sensor response in terms of the dc electric resistance on exposure to ammonia. The change in resistance is found to decrease linearly with NH_3 concentration up to 58 ppm and saturate thereafter [33]. The decrease in resistance is explained on the basis of removal of a proton from the acrylic acid dopant by the ammonia molecules, thereby rendering free conduction sites in the polymer matrix.

Electroactive nanocomposite ultrathin films of polyaniline (PANI) and isopolymolybdic acid (IPMA) for detection of NH_3 and NO_2 gases have been fabricated by alternate deposition of PANI and IPMA following Langmuir–Blodgett (see later) and self-assembly techniques [34]. While the NH_3 -sensing involves de-doping of PANI by basic ammonia, in NO_2 sensing NO_2 plays the role of an oxidative dopant, causing an increase in the conductivity.

For optical pH sensors based on PANI, the effect of pH on the change in electronic spectrum of the polymer is explained by the different degree of protonation of the imine nitrogen atoms in the polymer chain [35]. For the quantitative analysis of ions in solutions by ion selective sensors (ISS), polymers have been utilized to entrap the sensing elements, the ion selectivity being conveyed by ionophore (e.g., ion-exchange agents, charged carriers, and neutral carriers) doped in polymeric membranes. Ion sensors find wide application in medical, environmental and industrial analysis. They are also used for measuring the hardness of water. Polyacetylene can be used for determining the concentration of nitrate ions in acid solutions because as a result of the intercalation oxidation the conductivity of the polymer changes. The use of conducting polymers for preparing enzymatic electrochemical microsensors sensitive to glucose content has been reported.

Polyaniline and its substituted derivatives, such as poly(*o*-toluidine), poly(*o*-anisidine), poly(*N*-methylaniline), poly(*N*-ethylaniline), poly(2,3-dimethylaniline), poly(2,5-dimethylaniline) and poly(diphenylamine) have been reported [36] to show measurable responses (sensitivity $\sim 60\%$) for short chain alcohols (viz., methanol, ethanol and propanol) at concentrations up to 3000 ppm. The change (decrease) in resistance of the polymers on exposure to alcohol vapors has been explained based on the vapor-induced change in the crystallinity of the polymer. Polypyrrole (PPy) incorporated with dodecyl benzene sulfonic acid and ammonium persulfate has been reported to show a linear change in resistance when exposed to methanol vapor in the range 87–5000 ppm [37]. The response is rapid and reversible at room temperature.

Conducting polymers such as polyfuran and polythiophene may have valuable uses in humidity sensors and radiation detectors as the conductivity of these doped polymers varies considerably when exposed to humidity or radiation.

PPy has been widely used for gas sensors and biosensors [38,39]. The physical and chemical properties of PPy depend strongly on the nature of the dopant anions and their interactions with other chemical species. Though thin films of PPy can be very easily made by electrochemical deposition, a challenge in their applications in thin film-based devices is that the active sensing components remain embedded in the bulk, which limits both the efficiency and the sensitivity. This can be improved by making PPy in a nanofiber form to generate high surface area for a given mass or volume, thus providing a large number of surface functional groups to which sensing chromophores or enzymes can be anchored [40]. Moreover, the nanofiber texture can enhance the transport of ions and chemicals from the solution to the interior of the sensor component.

The production of PPy in a nanofiber form has been traditionally accomplished through templated synthesis methods which employ mesoporous silica, anodized aluminum oxide membrane, and particle track-etched membranes [41–43], while a bulk growth approach using V_2O_5 seed as a template has been reported more recently [44]. However, nanofibers produced by these methods are typically very short and not easy to handle for device fabrication. An electrospinning technique has thus been widely used for producing polymeric nanofibers in a nonwoven mat that is amenable to handling macroscopically [45]. (Note: Electrospinning is a process that produces continuous polymer fibers through the action of an external electric field imposed on a polymer solution. For a review of the process see previous publications [45–47].)

Nanofibers can also be deposited directly on device substrates. Polyaniline being soluble, the electrospinning process has been successfully utilized for the production of polyaniline nanofibers [48]. However, this process cannot be directly employed for producing PPy nanofiber due to the intractability of PPy.

To overcome the problem of intractability of PPy, a simple two-step process has been reported recently [49] for the synthesis of electrically conducting PPy nanofibers. The method consists of electrospinning of poly(ethylene oxide) (PEO) nanofibers that contain Fe(III) oxidants, followed by vapor phase polymerization of pyrrole. PEO is chosen as it forms a complex with FeCl_3 , which is known to be one of the most efficient oxidants for pyrrole polymerization and leaves chloride ions in the produced PPy making it electrically conducting. Since the Fe^{3+} ions are bound by the coordinating oxygen atoms of the PEO chains, it suppresses crystallization of FeCl_3 and ensures homogeneous distribution of FeCl_3 , and hence of the produced PPy, along the PEO nanofibers as PPy is produced by the vapor phase polymerization [50] through diffusion of pyrrole monomer into the FeCl_3 -containing PEO nanofibers.

In a typical process [49], a homogeneous solution of PEO- FeCl_3 (10.7 wt.%) prepared by dissolving a mixture of PEO and FeCl_3 (1:2.5 by weight) in a solvent consisting of ethanol and water (1:2.3 by weight) is loaded into a glass pipette (Figure 5.26) and a positive bias of 8 kV is applied to the solution. The electrospun fibers are collected on a ground electrode (aluminum foil) placed ~ 10 cm from the glass pipette tip. The electrospun PEO- FeCl_3 nanofibers are then exposed to pyrrole vapor at ambient conditions (8.3 torr at 25°C), the exposure time varying from 1 to 14 d for vapor phase polymerization to take place. The sheet conductivity of the as produced PPy-PEO composite nanofiber (average diameter 96 nm) mat at room temperature is in the order of $10^{-3} \text{ S.cm}^{-1}$ [49].

5.4.2.3.4 Microelectronics

Inherently conducting polymers offer a unique combination of properties that make them attractive for use in microelectronics [51]. The conductivity of these materials can be tuned by chemical manipulation of the polymer backbone, by variation of the dopant and degree of doping, and by blending with other polymers. In addition, they offer the advantages of light weight, processability, and flexibility. The conducting polymers have potential for use in an array of microelectronic applications ranging from the device level to the final electronic product.

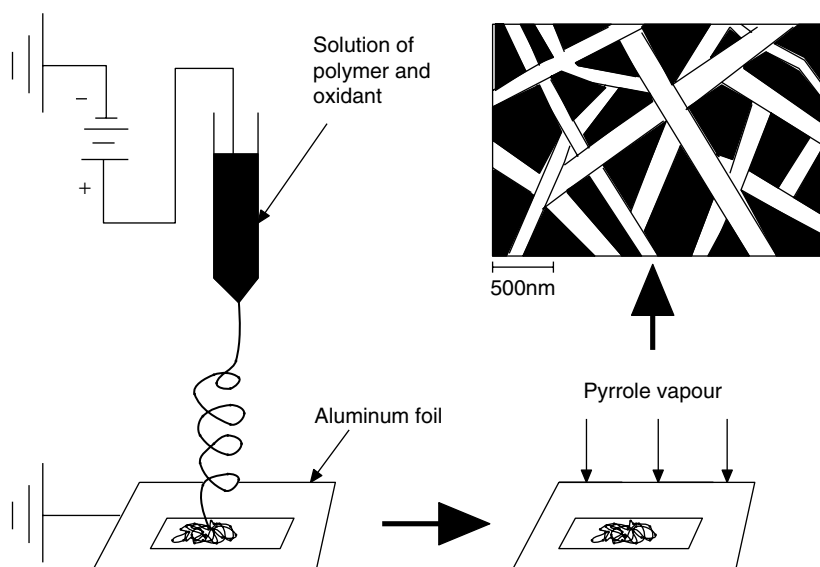


FIGURE 5.26 Schematic of electrospinning of PEO nanofiber templates containing FeCl_3 followed by vapor phase polymerization of pyrrole. An SEM image of the resulting PPy-PEO composite nanofibers is shown at top right corner. The scale bar for the image is about 500 nm. (After Nair, S., Natarajan, S., and Kim, S. H. 2005. *Macromol. Rapid Commun.*, 26, 1599. With permission.)

During the e-beam patterning process, charging of the resist is a significant problem. Thick insulating resist materials can trap charge and the trapped charge can deflect the path of the e-beam, resulting in image distortion as well as level-to-level registration errors. To eliminate this problem, conducting materials are incorporated into resist systems (see later) as coatings above or below the imaging resist to function as discharge layers. Intrinsically conducting, in particular the soluble, derivatives are attractive charge dissipators for e-beam lithography. These materials combine high conductivity with ease of processability. The first conducting polymer to be used in this type of application is polyaniline.

IBM introduced a family of polyanilines, referred to as PanAquas™, which are highly soluble in neutral water in the conducting form. The PanAqua provides a simple and effective discharge layer for e-beam lithography and can be cleanly removed during the alkaline development of the resist. A water-soluble polythiophene derivative referred to as ESPACER (a trade mark and product of Showa Denko K. K.) is also very effective at eliminating resist charging and can be removed by water wash.

A method used to prevent charging of the sample during scanning electron microscopic inspection is to coat the sample with a conducting metal such as gold, which is a destructive process as the metal cannot be removed from the surface of the substrate. Conducting polymers that can be spin-applied onto the sample and subsequently removed cleanly are ideal. Polyaniline has been demonstrated to provide such a solution.

In microelectronics, metallization generally refers to the deposition of a patterned film of conducting material on a substrate to form interconnections between electronic components. Conducting polymers have been demonstrated to provide a new route to metallization, in particular in PCB technology [52]. The conducting polymers that have been of interest in this area include polyaniline, polypyrrole, and polythiophene.

The fact that many conducting polymers are semiconductors in the undoped or slightly doped state has prompted attempts by both industrial and academic groups to use them in microelectronics such as in semiconductor devices and especially field effect transistors (FETs) [53]. For a FET's active layer, i.e., semiconducting layer between the source and drain electrodes, micrometer-thick films are required. Film as thin as this has been prepared by spin coating a solution of a precursor polymer on a substrate having the required electrode pattern and subsequent heat treatment in a stream of gaseous dopant to convert it into a conducting polymer. Improvement of technique has led to carrier mobilities as high as $10^{-1} \text{ cm}^2/\text{V}\cdot\text{s}$ in polymeric FETs. This has opened the way to uses such as flat-panel color displays for computers and possibly flat color televisions when tied to a liquid crystal matrix.

Electroluminescence from semiconducting conjugated polymers was first reported in 1990 [54] using poly(*p*-phenylenevinylene) (PPV) as the single semiconductor layer between metallic electrodes, as illustrated in Figure 5.27. PPV has energy gap between π and π^* states of about 2.5 eV and produces

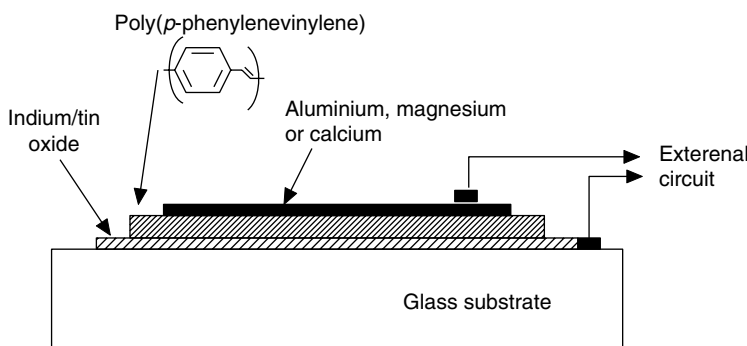


FIGURE 5.27 Schematic structure of a single-layer polymer LED device formed with poly(*p*-phenylene vinylene). (After Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burn, P. L., and Holmes, A. B. 1990. *Nature*, 347, 539.)

luminescence in a band below this energy. Light emitting diodes (LEDs) have been fabricated from PPV as the emissive layer. Operation of an LED is achieved when the diode is biased sufficiently to achieve injection of positive and negative charge carriers from opposite electrodes. Capture of these oppositely charged carriers in the polymer layer can result in the formation of singlet exciton, which is generated by photoexcitation across the π - π^* gap and this can then decay radiatively to produce the same emission spectrum as that produced by photoexcitation.

Further advances in the chemistry of processible conjugated polymers and focused work on the physics of electroluminescence in these materials have led to the development of flexible, almost entirely metal-free LEDs [55]. These polymer-based LEDs could be competitive in display applications because of the potential ease, low cost of fabrication, and large surface area of devices based upon processible polymers.

5.4.2.3.5 *Electrostatic Discharge Protection*

Electrostatic charge (ESC) and electrostatic discharge (ESD) are a serious and expensive problem for many industries, in particular for microelectronics. Electrostatic charge can accumulate to thousands of volts and discharge in the form of a lightning bolt, which can destroy devices on ICs. To protect devices against ESC and ESD, conducting materials are extensively used. The materials currently used include ionic conductors, carbon- or metal-filled resins and in certain cases metal coatings. They do not offer the ideal solution to ESD protections. Ionic conductors, though inexpensive, have significant drawbacks, such as very low surface conductivity (10^{-9} – 10^{-11} ohm⁻¹/square) and so are not dissipative. Moreover, the conductivity is humidity dependent, as water is needed for ionic conduction. Carbon-filled systems, on the other hand, pose contamination concerns due to sloughing of carbon particles.

Intrinsically conducting polymers offer a new alternative to these materials for ESD protection with numerous advantages. The conductivity can be tuned and can easily meet the high end of the dissipative range. In addition, conducting polymers can offer a high degree of transparency. Polyaniline, polypyrrole, and polythiophene have been the predominant conducting polymers of interest for ESD protection. Doped polyaniline in the form of a dispersible powder (Versicon, a trademark of Allied-Signal Corp.) has been blended with a number of thermoplastic and thermoset resins to achieve excellent ESD properties [56].

Of particular interest for ESD protection of electronic component packages are coating formulations. The coating can be applied directly onto already fabricated packages by spray-coating, or they can be applied onto plastic sheets that are subsequently thermoformed into a package. One type of coating is based on dispersions of doped polyanilines. Versicon coatings based on soluble polyanilines have also been produced. One such system is a curable water-based coating reported by IBM [24]. An aqueous coating based on a poly(3,4-ethylene-dioxythiophene)/polystyrenesulfonic acid blend is reported to exhibit antistatic properties [57].

5.4.2.3.6 *Other Applications*

Development of electrically conducting polymers that can be processed as thermoplastics and possess the advantageous mechanical behavior and corrosion stability of plastics would open up entirely new fields of applications. Some of the many applications in which electrically conducting polymers would find a large market are cables and conducting electricity, wall papers that allow electrical heating, materials for antistatic equipment, and conducting fabrics.

The polymerization and doping of conducting polymers on such fabrics as nylon, polyester, and cotton to produce fabrics with a range of conductivities under the trade name Context has been achieved by Milliaken and Co., Spartanburg, S.C. These materials are under intensive study for use in aircraft and tanks of the future. They could also be used for heated clothing, protecting computers against EMI, static dissipation in high speed missiles, and conveyor belts to handle static-sensitive electronic and flammable goods.

Electrically conducting polymers are also regarded as promising candidates for use as passivating layers with respect to photocorrosion of photoelectrodes. For example, films of polypyrrole have been tested as coating for certain semiconductor electrodes.

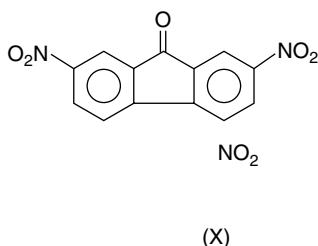
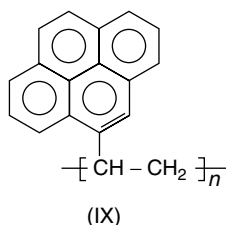
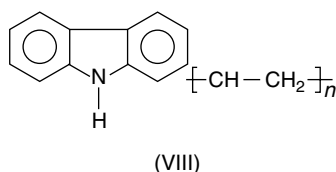
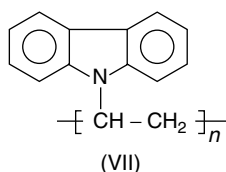
Structures similar to muscle fibers have been proposed by researchers in Japan and Italy. They are based on the property that a conducting polymer in a fiber from undergoes dimensional changes due to expansion and contraction along the fiber's length as a result of electrochemical doping and undoping.

Other possible applications include conductive paints, toners for reprographics and printing, and as components for aircraft where the combination of light weight, mechanical strength, and moderately high conductivity are required.

Recently, electrically conductive fiber composites have been prepared from polypyrrole-engineered pulp fibers [58]. To prepare such fibers, FeCl_3 solution is first dispersed into pulp, which is disintegrated by kneading and stirring. The dopant (anthraquinone-2-sulfonic acid, sodium salt) slurry and pyrrole solution are then added to start the polymerization, the molar ratio of FeCl_3 to pyrrole and that of dopant to pyrrole being 3:1 and 1:3, respectively, for the optimum effect. Paper composites can be prepared both directly from the modified pulp fibers and by adding the modified fibers as conductive-fiber fillers into the paper making stock. For the latter method, less monomer (i.e., conductive polymer) is needed to achieve the same level of conductivity while a higher tensile strength in the paper is attained, as compared to paper obtained exclusively from treated fibers.

5.4.3 Photoconductive Polymers

The enhanced flow of current under the influence of an applied electric field that occurs when a semiconductor is exposed to visible light or other electromagnetic radiation is known as photoconduction. Poly(*N*-vinyl carbazole) (VII) and various other vinyl derivatives of polynuclear aromatic compounds such as poly(2-vinyl carbazole) (VIII) and poly(vinyl pyrene) (IX) have high photoconductive efficiencies. The excellent photoconductivities of these polymers are believed to be due to their helical conformation with successive aromatic side chains lying parallel to each other in a stack along which electron transfer takes place relatively easily.



Poly(*N*-vinyl carbazole) absorbs light in the 360 nm region to undergo electronic excitation and ionization in the electric field. The photogeneration efficiency of the polymer can be greatly enhanced by the addition of an equimolar amount of 2,4,7-trinitrofluorenone (TNF) (X), which shifts the absorption of poly(*N*-vinyl carbazole) into the visible range by the formation of a charge transfer state, rendering it photoconductive at 550 nm. While the polymer alone is a hole conductor, the addition TNF creates electron carriers and the conduction mechanism actually becomes electron dominated.

Photoconduction forms the basis of electrophotography. In this photocopying process, or xerography as it is sometimes known, a photoconductive material is coated onto a metal drum and uniformly charged (sensitized) in darkness by a corona discharge. The drum is then exposed to the bright image of

the object to be copied whereupon the illuminated areas of the photoconductive material become conductive and dissipate their charge to the metal drum (earthed). The photoconductive material in the dark areas is still charged and so is able to attract a positively charged black resin-coated toner powder forming a latent image of the object. The latent image is then transferred to a piece of negatively charged paper which is heated to fuse and fix the resin, thereby making the image permanent.

Early photoconductive materials were based on selenium compounds such as As_2Se_3 . Such a material is difficult to handle, because it needs to be applied by vacuum sublimation and it is rather brittle. Poly(*N*-vinyl carbazole)-based materials are now replacing the selenium-based compounds.

Much work has been reported on the development of carbazole derivatives and also noncarbazole photoconductive polymers. An example of the latter group is poly(bis(2-naphthoxy)phosphazene), which is intrinsically an insulator with a very low photosensitivity toward both UV and visible radiation, but when doped with trinitrofluorenone in a 1:1 molar ratio, it is a strong photoconductor.

5.4.4 Polymers in Fiber Optics

Polymeric optical fibers (POFs) combine the benefits of all optical fibers with additional amazing simplicity in handling. This is mainly due to their relatively large diameter and acceptance angle (or numerical aperture). In spite of the outer diameter being typically in the range of 1 mm, the fiber remains flexible because of the polymer material used, mainly acrylics PMMA. These benefits make POF attractive for a wide variety of under-water, indoor and outdoor lighting, data transmission, and sensor application. The fiber optic cable or tube employs the phenomenon of total internal reflection (see [Piped Lighting Effect, Chapter 3](#)) to carry the light throughout the length of the cable.

In construction, POF cable is made up of a light carrying solid polymer core with a thin protective coating, or covering, called the cladding. The light entering the fiber optic tube is trapped within the core and is continually reflected as it moves down the path, the interface between the core and the cladding of the tube wall acting like a mirror. The light comes out of the other end or is diverted. A less common type of fiber optic cable, called a side-emitting fiber, distributes the light along the entire length of the tubing like neon lighting.

In its simplest form, a fiber optic lighting system consists of an illuminator or light source, and a number of fiber optic cables or light guides that carry the concentrated beam of light produced by the light source ([Figure 5.28](#)) [59]. The illuminator can use a filter to remove most of the lamp's infrared and ultraviolet energy that may damage and fade the colors in textiles, paintings and graphic art pieces.

Originally conceived as a means of lighting pools and fountains, the fiber optic technology has since been embraced by lighting architects for several indoor uses due to its low heat production. As the fiber optic lighting does not create electromagnetic fields, this lighting technology can be used in areas with EMF-sensitive electronic equipment, such as magnetic resonance imaging (MRI) room.

As every other optical fiber, POF has a core-cladding structure as shown in [Figure 5.29](#). In most cases, the core material (diameter 980 μm) is highly purified PMMA with a typical refractive index, $n_1 = 1.49$, coated with a cladding (thickness 10 μm) of fluorinated polymer with typical refractive index, $n_2 = 1.42$, while the polymers used for sheath/jacket are PE, HDPE, PVC, and nylon. The numerical aperture (NA) thus has a value of 0.50. With this high NA the bandwidth is limited to theoretical values of some 10 Mbit/s. Since the bandwidth is related to the fiber NA, the transmission capacity can be increased by lowering the NA. However, lowering NA causes increased bending sensitivity. A trade-off has therefore to be found for the optimum POF for a specific application.

As large core POFs suffer from sensitivity to bending, these losses can be reduced by using multiple small cores [[Figure 5.30\(a\)](#)] instead of a single large one. The problem can also be overcome by using the so-called double-step-index fibers [[Figure 5.30\(b\)](#)] as an intermediate step to multi-step-index fibers.

The best solution achieved so far for obtaining high bandwidth with large core diameter is using a graded index profile [[Figure 5.30\(c\)](#)]. Since more than 15 years a lot of progress has been made in shaping the profile by different methods. Until 1996, mainly PMMA has been used as the core material which had

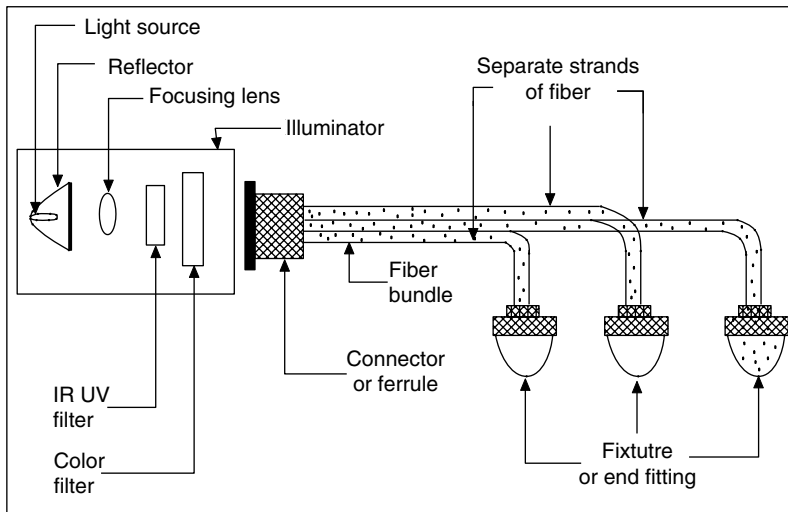


FIGURE 5.28 Schematic representation of a fiber optic lighting set-up. (After Knisley, J. 2002. Fiber optic lighting dries out, ecmweb.com/mag/electric_fiber_optic_lighting.)

to be doped or polymerized differently. However, a new product has now reached the market. It is Lucina[®] (120 μm core diameter) fiber made out of CYTOP[®], offering low attenuation combined with high bandwidth, but giving up the specific benefits of large core diameter [60].

The application of POF for data communication over short distances is quite old. Thus, cables connecting HiFi set-ups or in industrial production lines are well known where the main reason for using POF was its complete immunity to EMIs. Much progress was made in 1980s when low loss polymers were developed and drawn into fibers starting with Step-index (SI) profile, followed by first attempts to

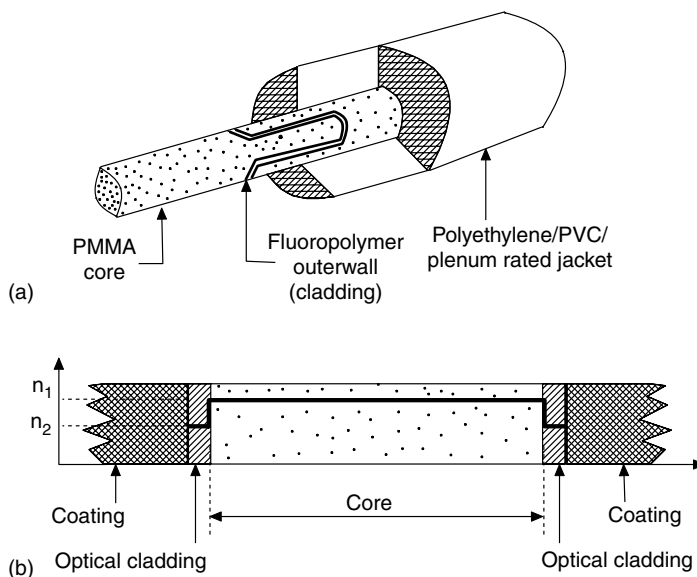


FIGURE 5.29 Standard PMMA step-index polymer optical fiber. (a) Structure of cable. (b) Refractive index (n) profile. (After Knisley, J. 2002. Fiber optic lighting dries out, ecmweb.com/mag/electric_fiber_optic_lighting.)

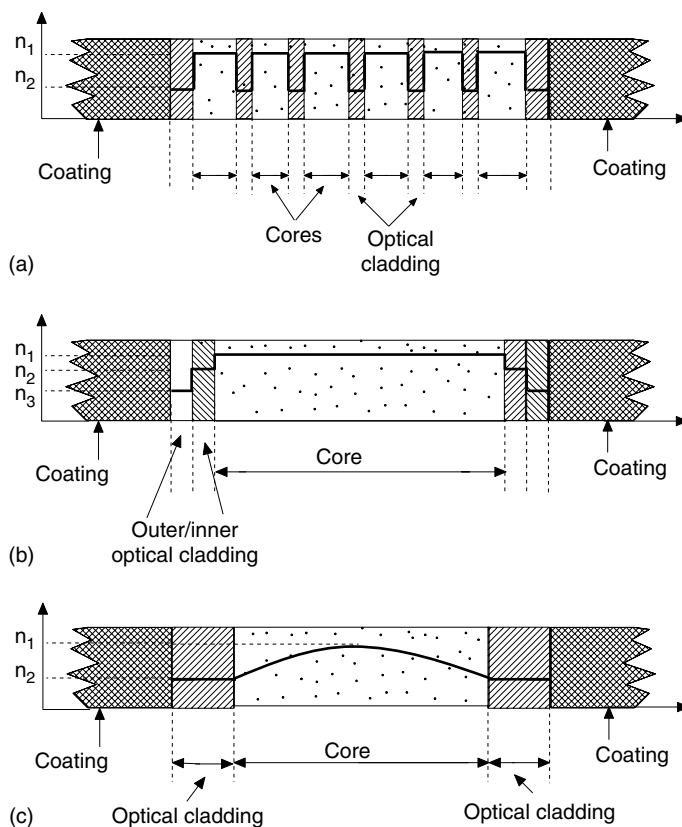


FIGURE 5.30 Refractive index (n) profiles of optical fiber cables: (a) multi-core step index fiber; (b) multi-step index fiber; (c) graded index fiber. (After Knisley, J. 2002. Fiber optic lighting dries out, ecmweb.com/mag/electric_fiber_optic_lighting.)

produce graded index (GI) profiles. From then on more rapid progress was made in the application of POF, as bandwidth and range increased every year and with the development of CYTOP[®] fibers, attenuation values in the range of high quality silica fibers could be reached.

The attenuation limit of PMMA, generally used as the core material of commercially available step-index polymer optical fiber (SI-POF), is approximately 100 dB/km in the visible region. This high attenuation of POF compared to the silica-based fiber (Figure 5.31) has limited the POF data link length, even when the bandwidth characteristics are improved by the graded index-POF (GI-POF) [61]. However, the perfluorinated (PF) amorphous polymer base GI-POF has a low loss wavelength region (Figure 5.31) from 500 to 1300 nm [62]. The experimentally observed total attenuation of PF polymer-based GI-POF decreases to 40 dB/km even in the near infrared region, while the theoretical limit is still lower (see Figure 5.31).

While silica based single mode optical fiber, because of its high bandwidth, is widely used in the long distance trunk area for giga bit per second transmission and beyond, the use of silica-based multi-mode fiber is a recent trend in the area of local area networks (LANs) and interconnection, because the large core diameter of the multi-mode fiber of 50 and 62.5 μm relaxes the tolerance required for connection compared with the single mode fiber whose core diameter is only 5–10 μm . However, even with the multi-mode silica fiber, an accurate alignment in the connection is still required. Compared to this, the large core diameter (100–1000 μm) of POF enables the use of inexpensive polymer connectors, prepared by injection molding, because even a displacement of $\pm 30 \mu\text{m}$ in the connection does not seriously

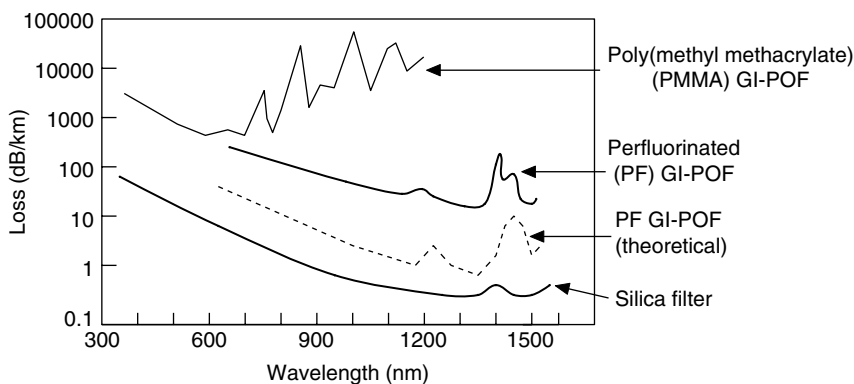


FIGURE 5.31 Attenuation of graded index polymer optical fiber in comparison with that of silica fiber.

influence the coupling loss [63]. Moreover, a large core of more than 100 μm could reduce the modal noise, which disturbs systems with multi-mode silica fibers [64].

There are many uses for POF, ranging from telecommunications to consumer electronics, in addition to conventional illumination systems based on fiber optic lighting [65]. POF is an ideal medium for short range networking, as it is easier to connect and has lower installation costs. With its ability to sustain smaller bend radius, POF is more user friendly and is able to withstand rigorous installation tasks such as pulling the fiber through walls and plenums. POF has potential applications in the aerospace industry since with its lighter weight it can replace the heavy copper wire or silica fiber now being used. Efforts are also being made to use fiber optics to channel light to instrument panels for increased brightness and reduced weight. Light weight, ease of use, and data transmission capabilities also make POF a perfect choice for consumer electronics and automobile applications where internet capability and other high data transfer features have started to make their entry. POF's tight bend radius, complete EMI immunity and low cost make it uniquely suitable for several image-transfer applications in medical industry. The primary advantages of POF over copper are increased bandwidth and durability. These properties make POF a cost effective replacement. Additionally, copper is prone to tapping and it is not a secure medium, whereas optical fiber is extremely difficult to tap.

5.4.5 Polymers in Nonlinear Optics

Materials that have nonlinear optical properties are of considerable interest because of their potential for optical switching and waveguiding applications in telecommunication [66–68]. Until recently, nearly all of the nonlinear optical materials commonly in use were inorganic solids. However, there is currently a growing interest in organic and polymeric solids because of their exceptionally large nonlinear, second-order optical properties and the larger variety of asymmetrical crystal structures available. Possible applications of these materials include amplifiers, frequency doublers, waveguides, Q-switches (used for building up power output in lasers) and fitters.

Nonlinear second-order optical properties include second harmonic generation and the linear electro-optic effect. Second harmonic generation is the ability of a material to double the frequency of light passing through it, and the linear electro-optic effect is a change in the refractive index of a material under the application of a low-frequency electric field. For these effects to occur, the material must not have a center of symmetry, while for maximum second harmonic generation, a crystal should possess propagation directions where the crystal birefringence cancels the natural dispersion, leading to the condition of equal refractive indices at the fundamental and second harmonic frequencies (phase matching).

Phase-matched second harmonic generation in single crystal polymers was first observed in 2-methyl-4-nitroaniline substituted diacetylene polymers. Subsequently, a number of other diacetylene structures

have been synthesized that exhibit orders of magnitude greater phase-matched second harmonic generation than lithium iodate.

Besides single crystals, disubstituted diacetylene polymer thin films can be obtained for waveguide applications by evaporation, solidification, or deposition of the diacetylene monomers by the Langmuir–Blodgett approach, which allows film thicknesses to be controlled at the molecular level. These diacetylene films can be patterned using selective polymerization techniques such as developed for UV, x-ray, and electron beam lithography.

5.4.6 Langmuir–Blodgett Films

The preparation of ordered thin films is of considerable interest in the construction of electronic devices and model membrane systems. A method that has gained much popularity in this area is the Langmuir–Blodgett (LB) technique [67]. The technique is based on the premise that molecules with a hydrophilic head and a hydrophobic tail can form a monolayer at an airwater interface and can be transferred onto a solid surface.

The process of film formation can be carried out either by dipping a glass slide (or some other substrate) vertically into a trough containing a monolayer on the surface, as shown schematically in Figure 5.32, or alternatively by using a rotating substrate to effect a horizontal transfer. Either way can be used to build up monolayers by one passage or multilayers by repeated passage of the substrate.

To make polymeric films one selects a molecule with a polymerizable unit (double or triple bonds) so that the mono- or multilayer films can be subsequently converted into a polymer structure by thermal treatment or exposure to UV or γ radiation. Several possible monomer structures are shown in Figure 5.33.

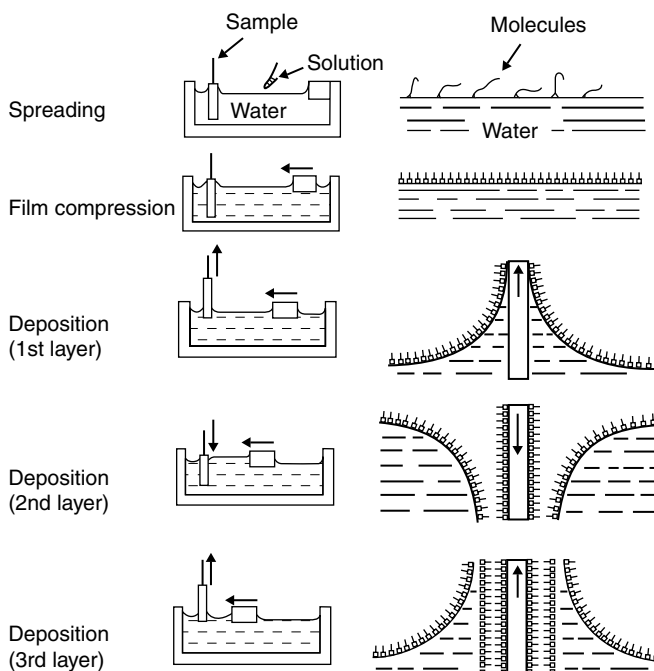


FIGURE 5.32 Schematic representation of the formation of mono-, bi-, and tri-layers of molecules from a Langmuir–Blodgett trough. (After Chemla, D. S. and Zyss, J. eds. 1987. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1, no. 4, Academic Press, San Diego, CA.)

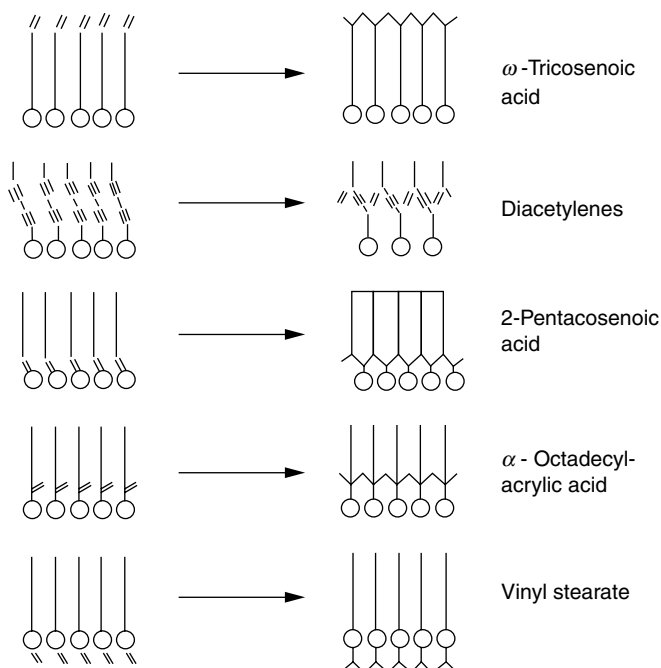


FIGURE 5.33 Schematic of possible monomer structures that can be polymerized in thin films formed using the Langmuir-Blodgett method.

Polyacetylenes containing suitable amphiphilic groups can be used to produce thin films in this way, e.g., heptadeca-4,6-diyne-1-ol and the corresponding acid. It has been found advantageous to use the neutralized form of acid derivatives. For example, diacetylene monocarboxylic acids generally form much more stable films if the cadmium salt is used initially; in this case, Cd^{2+} ion remains in the aqueous phase as a counterion.

Ordered thin films prepared by the Langmuir-Blodgett method have found application in nonlinear optics. The method has also been applied in nanolithography. The miniaturization of integrated circuits requires high resolution, and for this purpose electron beams are used. To improve pattern definition on the resist (discussed later) used in this application, it is necessary to employ much thinner resist films and shorter exposure times. In this respect, thin LB films are superior to conventional spin coating since the latter technique does not always guarantee that the resist film will be free from defects such as pin holes that can spoil the subsequent pattern. Improved resolution has been obtained, for example, from resists prepared using polymerized ultrathin (45 nm) LB films of ω -tricosenoic acid, $\text{CH}_2=\text{CH}(\text{CH}_2)_{20}\text{COOH}$, and α -octadecyl acrylic acid $\text{CH}_2=\text{C}(\text{C}_{18}\text{H}_{37})\text{COOH}$. The LB technique holds great promise in the area of molecular electronics, where precise control of the molecular structure is of paramount importance.

5.4.7 Piezo- and Pyroelectric Polymers

Piezoelectricity is defined as an electric polarization that occurs in certain crystalline materials at mechanical deformation [69]. The polarization is proportionate to the deformation and the polarity changes with change in deformation. In reverse, electric polarization produces mechanical deformation in piezoelectric crystals. The piezoelectric materials also possess pyroelectric properties, i.e., electric polarization is generated at temperature change.

If a polymer has a larger dipole moment in its molecule than can be aligned to form a polar crystal, there is every likelihood it will exhibit strong piezo- and pyroelectricity. However, though many polar

polymers such as poly(vinyl chloride), polyacrylonitrile, and nylon- 11 have relatively large dipole moments, they exhibit only weak piezoelectric activities because the dipoles cannot be aligned very well by an electric field.

A major advance was made in 1969 when a strong piezoelectric effect was discovered in poly(vinylidene fluoride) (PVDF). The effect is much greater than for other polymers. In 1971, the pyroelectric properties of PVDF were also first reported, and as a consequence, considerable research and development has continued during the last two decades.

Poly(vinylidene fluoride) is a semicrystalline thermoplastic polymer consisting of $(-\text{CH}_2\text{CF}_2-)$ units in long chains. The crystallinity is normally about 55%, and the polymer forms lamellar crystals typically 10 nm thick by 100 nm long that are dispersed in an amorphous phase that has a glass transition temperature of about 40°C. The molecule, which may extend through several crystalline and amorphous regions, can have three morphological forms known as α , β , and γ -PVDF.

The preferred form for piezoelectric activity is the β -PVDF, which has all-trans conformation (Figure 5.34) with dipoles essentially normal to the molecular axis. The α -PVDF, on the other hand, has trans-gauche-trans-gauche ($\text{tg}^+ \text{tg}^-$) conformation (Figure 5.34) having components of the dipole moment both parallel and perpendicular to the chain axis. When packed in the respective unit cells, the dipoles of the chain interact in form β giving a large dipole moment, but are antiparallel in form α . In order to obtain strongly piezoelectric (pyroelectric) PVDF, the nonactive α -form must therefore be converted to the active β -form. This may be done by special treatment during the extrusion process.

In order to impart stronger piezoelectric properties to PVDF, a number of processing steps are undertaken. The material is uniaxially stretched at 150°C and annealed and then subjected to *poling* a

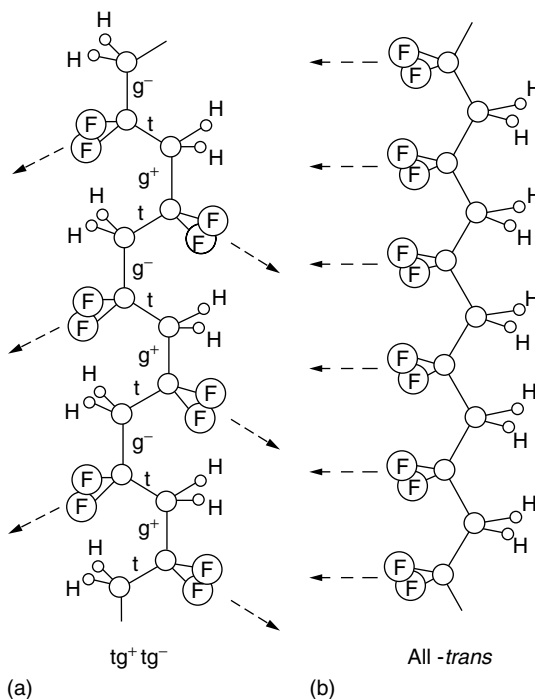


FIGURE 5.34 Schematic presentation of the two most common crystalline chain conformations in PVDF: (a) $\text{tg}^+ \text{tg}^-$ (α form) and (b) all-trans (β form). The arrows indicate projections of the $-\text{CF}_2$ dipole directions on planes defined by the carbon backbone. The $\text{tg}^+ \text{tg}^-$ conformation, where t=trans, and g=gauche, and g⁻=gauche minus, has components of the dipole moment both parallel and perpendicular to the chain axis. The all-trans conformation has all dipoles essentially normal to the molecular axis.

term used to describe methods of inducing polarization), either thermally or by a corona discharge procedure.

In the case of thermal poling, electrodes are evaporated on to the PVDF and a field of 0.4–1.4 MV/cm is applied at temperatures of 90–100°C for 1 hr. Cooling with the field maintained stabilizes the polar orientation of the crystallites and produces permanent polarization (poling).

For corona poling, which is a faster method used industrially, the nonmetallized or half-metallized PVDF film is subjected to a corona discharge from a needle electrode a few centimeters away. The resulting charge buildup on the film generates a field in the sample that is sufficient to align the polar chains, even at room temperature. A very high piezoelectric activity can be obtained by a combination of stretching and corona poling.

The parallel dipolar alignment in PVDF film treated as above leads to a residual polarization, which is the basis for several proposed mechanisms that explain the piezoelectric and pyroelectric behavior of the material. Although various observations support the suggestion that PVDF is also ferroelectric, its Curie point has not been detected. (Most ferroelectrics show a phase transition at a temperature known as the *Curie point* above which they become paraelectric.)

PVDF film, as produced from the melt, is largely in the nonpolar α -form, the β phase only being obtained after subsequent processing operations, as described above. If however, vinylidene fluoride is copolymerized with as little as 7% by weight of trifluoroethylene, a copolymer is formed with crystallites completely in the β -form. This obviates the need for stretching after synthesis and the copolymer can be processed by way conventional routes, such as injection molding. Moreover, unlike PVDF, copolymers of vinylidene fluoride and trifluoroethylene have been shown to demonstrate the ferroelectric to paraelectric transition. For a copolymer with a composition of 55% vinylidene fluoride and 45% trifluoroethylene, a phase transition is observed near 70°C, and with 90% vinylidene difluoride, a phase transition at 130°C.

5.4.7.1 Applications

Technological applications exist for both the piezo- and pyroelectric phenomena, but piezoelectric applications are the most common. Piezoelectric materials are of practical importance because they permit conversion of mechanical energy into electrical energy and vice-versa. Compared to inorganic piezoelectric material, the great advantages of piezoelectric polymers lie in their workability, mechanical flexibility, high shock resistance, low cost, low density, chemical stability, and availability in large sizes.

A large number of applications have been proposed for piezoelectric polymers. The types of applications can be grouped into five major categories: sonar hydrophones, ultrasonic transducers, audio-frequency transducers, pyroelectric sensors, and electromechanical devices. The principal polymers of interest in these applications are PVDF and copolymers of vinylidene fluoride and trifluoroethylene.

The greatest use of PVDF is as a source of pressure. The fact that PVDF has an acoustic impedance that is close to that of water or the human body makes it especially suitable as a source of pressure in underwater technology and medicine. PVDF also has an extreme band width, i.e., a large frequency range.

With its low acoustic impedance, extreme band width, high piezoelectric coefficient, and low density (only one-quarter the density of ceramic materials), PVDF is ideally suited as a transducer for broad band underwater receivers in lightweight hydrophones. The softness and flexibility of PVDF give it a compliance 30 times greater than ceramic. PVDF can thus be utilized in a hydrophone structure using various device configurations, such as compliant tubes, rolled cylinders, discs, and planar stacks of laminated material.

A 100 element 360° scanning sonar transducer utilizing PVDF has been developed by Marconi to provide a 360° view of the acoustic scene on a radar type display. Hydrophones for submarine reconnaissance are of great interest to the military. A comparison between PVDF and a ceramic material PZT-4 commonly used in sources of pressure is shown in [Table 5.12](#). The so-called g - d product, which is considered to be the standard of suitability for hydrophone applications, is 2.5 times greater for PVDF as

TABLE 5.12 Comparison of the Properties of PVDF-Film (Kureha 19) with Typical Values of PZT-4 Ceramic for Hydrophone Applications

Property	Units	PVDF Polymer	PZT-4 Ceramic
Piezoelectric constant—field/stress	10^{-3} Vm/N	174	11.1
Piezoelectric constant—charge density/stress	10^{-12} m/V	20	123
<i>g</i> - <i>d</i> product	10^{-12} m ² /N	3.48	1.37
Piezoelectric coupling factor	—	0.102	0.334
Relative dielectric constant	—	13	1300
Elastic compliance	10^{-12} m ² /N	330	10.9
Density	10^3 kg/m ³	1.78	7.5

Source: Wirsen, A. 1987. *Electroactive Polymer Materials*. Technomic, Lancaster, PA.

compared to the corresponding value for PZT-4. PVDF is thus superior for acoustical recording in water. Basic constructions of hydrophones with various sensitivity and pressure resistance are shown in Figure 5.35.

There is much interest in the application of PVDF in medical imaging because of its close acoustic impedance match with both tissues. Monolithic silicon-PVDF devices have been produced in which a sheet of PVDF is bonded to a silicon wafer containing an array of metal oxide semiconductor field effect transistor (MOSFET) amplifiers arranged in such a way that when an acoustic wave is detected, the electrical signal resulting from the piezoelectric action in the PVDF appears directly on the gate of an MOS transistor. The device is therefore known as a piezoelectric oxide semiconductor field effect transistor (POSFET).

PVDF is generally an ideal material for transducers operating at frequencies above 0.5 MHz in hydrophones and pulse echo probes for medical and nonmedical testing. A 64-element linear array transducer has been produced that, operating at 5 MHz, offers a wide-bandwidth pulse response, sharp ultrasonic field distribution, and a high energy conversion efficiency.

While PVDF has piezoelectric properties similar to those of piezoelectric ceramic materials, the pyroelectric coefficient is too low to be useful except for specialized applications where the main

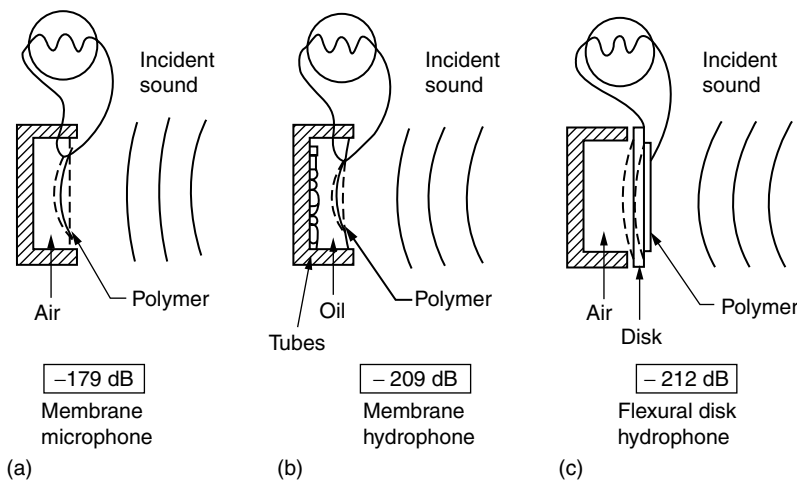


FIGURE 5.35 Cross-sections of cylindrical piezoelectric polymer receivers. (a) Membrane microphone formed by fixing a taut film over an air-filled cylindrical chamber. (b) Membrane hydrophone with an oil-filled chamber containing plastic compliant tubes to provide compliance while withstanding hydrostatic pressure. (c) Flexural disk hydrophone backed by air. The disk both excites the polymer film and provides strength against hydrostatic pressure.

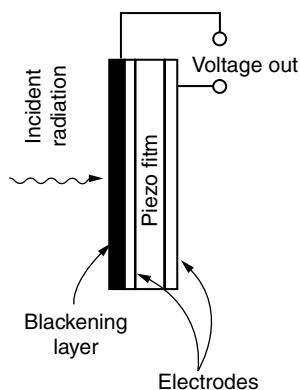


FIGURE 5.36 A pyroelectric detector made with piezo film.

requirements may be speed and resolution, and sensitivity is a minor consideration. PVDF, for example, has been used to form an array of 50 detectors for the energy profile determination of various wavelength laser beams. PVDF has also been employed in a pyroelectric vidicon to obtain a high resolution picture, because its low thermal conductivity reduces thermal spreading.

Pyroelectric detectors made with piezo films can be used in a number of specialized applications. A pyroelectric detector shown in Figure 5.36, consists of a thin semitransparent electrode placed on the front of the piezo film and a highly reflective rear electrode. A blackening layer added to the front electrode results in far more efficient broadband absorption

of incident radiation. The incident radiation passes into the piezo film, which absorbs strongly in the wavelength range of 8–11 μm . Pyroelectric detectors made with piezo film are used in intrusion detection systems and energy management systems. Pyroelectric detectors can also be used for humidity monitoring and certain gas detection, a good example being carbon monoxide.

Much interest has been shown in the use of PVDF for elements in telephone handsets. Plessey Telecommunications have produced bimorph microphone units using PVDF. It has also been employed in high fidelity tweeters and headphone transducers for audio applications.

5.4.8 Polymeric Electrolytes

The organic solvents currently used the most, tetrahydrofuran and propylene carbonate, have clear limitations in regards to stability [70–73]. The potential at which *p*-doping (indiffusion of negative ions) of polyacetylene electrode occurs is close to the anodic limit for propylene carbonate and higher than the limit for tetrahydrofuran. Thus one of the major problems with polymeric batteries is the problem of slow electrochemical breakdown of organic solvents at actual doping potentials.

An alternative to employing liquid electrolytes is to use a solid electrolyte to produce an all solid battery. This may have several advantages—an absence of electrolyte leakage or gassing, the likelihood of an extremely long shelf-life, and the capability of operating over a wide temperature range.

Polymeric materials, because of their low weight and ease of fabrication, have been investigated as electrolytes for lithium batteries. Early investigations included ion-exchange membranes, such as polystyrene sulfonic acid. However, it was found that in the dry state, the conductivity of these materials was extremely low (10^{-12} – 10^{-15} $\text{ohm}^{-1}\text{-cm}^{-1}$), and the addition of aprotic solvents, such as propylene carbonate, did not appreciably loosen the ionic clusters formed within these membranes.

Polymer gels based on polymers such as poly(vinylidene fluoride), polyacrylonitrile, and aprotic solvents containing added alkali metal salts, gave appreciable room-temperature conductivity. However, solvent volatility and voltage stability of the electrolyte were serious problems.

A new perspective in polymer electrolytes was obtained in 1978 when Armand [70] suggested the use of PEO-alkali metal salt complexes for alkali metal rechargeable batteries. Poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) form ion complexes with, for instance, NaI, NaBF_4 , LiClO_4 , LiCF_3SO_3 , and others. Perhaps the most important advantage of such polymer electrolytes is the ability of the complex to form a good interface with solid electrodes, thereby permitting faster kinetics at the ion transfer between electrode and electrolyte.

Figure 5.37 shows the structure of the PEO-salt complexes proposed by Armand. The regular PEO helix is filled by metal ions (M^+) solvated by ether oxygens, and the counterions (X^-) are expelled from

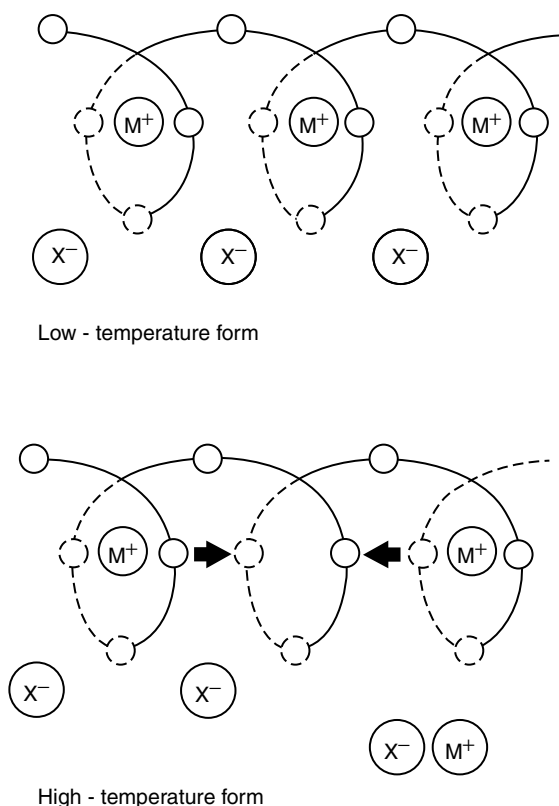


FIGURE 5.37 Proposed helical structure of PEO-salt complexes.

the strands of the parallel helices. (Pure PEO has a helical structure in the crystalline state with seven $\text{CH}_2\text{CH}_2\text{O}$ units in two turns of the helix.)

Initial measurements carried out on PEO-alkali metal salt complexes indicated that the observed conductivities were mostly ionic with little contribution from electrons. It should be noted that the ideal electrolyte for lithium rechargeable batteries is a purely ionic conductor and, furthermore, should only conduct lithium ions. Contributions to the conductivity from electrons reduces the battery performance and causes self-discharge on storage. Salts with large bulky anions are used in order to reduce ion mobility, since contributions to the conductivity from anions produces a concentration gradient that adds an additional component to the resistance of the electrolyte.

Though the conductivity of the PEO-alkali metal complexes ($10^{-3} \text{ ohm}^{-1}\text{-cm}^{-1}$ at 140°C) is fairly low in comparison with inorganic solid electrolytes such as β -alumina(Na), $\text{RbCu}_{16}\text{I}_7\text{Cl}_{13}$ and RbAg_4I_5 at the same temperature, this can be compensated for by the facile production of thin films typically 25–500 μm thick. A cell may thus consist of a lithium or lithium-based foil as anode, an alkali metal salt-PEO complex, such as $(\text{PEO})_9 \text{LiCF}_3\text{SO}_3$ (25–50 μm), as the electrolyte, and a composite cathode (50–75 μm) containing a vanadium oxide (V_6O_{13}) as the active ingredient. The vanadium oxide is one of a number of “insertion” compounds that permits the physical insertion lithium ions reversibly into their structure and thus allows recharging of the cell.

To function as an effective polyelectrolyte, the polymer should have a low glass transition temperature to allow the freedom of molecular movement necessary for ion transport. While the advantages of PEO-alkali metal complexes are their good electrochemical stability as well as faster kinetics at the ion transfer between electrode and electrolyte, the disadvantage is the low conductivity of the polymeric electrolyte at normal operating temperatures. Thus, in order to obtain high-power densities, it is necessary to work

at relatively high temperatures ($\sim 120^\circ\text{C}$). Although this temperature of operation may be suitable for certain application, for example, vehicle traction, quite clearly it would be unsuitable for other applications, such as consumer products.

Recently, a new polymeric electrolyte consisting of polyester-substituted polyphosphazene [71] has been developed. This polymer, which is designated MEEP, forms complexes with a large number of metallic salts, the complexes having a higher conductivity at room temperature than earlier polymer electrolytes. For example, MEEP- LiF_3SO_3 has a conductivity of $10^{-4} \text{ ohm}^{-1}\text{-cm}^{-1}$, which is sufficient for battery use, since the polymeric electrolyte can be shaped as films between the electrodes. This holds promise of very light batteries with potentially very great energy density.

While it is possible that future polymeric batteries will be all-polymeric solid-state batteries, it is predicted, however, that the most promising solid state batteries will combine polymeric electrolytes with nonpolymeric electrode materials such as TiS_2 , V_6O_{13} , Li or LiAl, the specific capacity of which surpasses that of polyacetylene electrodes.

As a great number of combination possibilities exist for electrode as well as electrolyte materials, the probability of developing rechargeable batteries with considerably increased performance may be considered to be high. For potential use in electric cars and other electrically operated vehicles, which may become an environmental requirement in densely populated areas, such developments in polymeric batteries are eagerly awaited.

Drastic improvement in rechargeable batteries is also of great interest militarily. One example is submarine batteries. Compared to lead-acid batteries, the polymeric batteries enjoy potential advantages in this area: faster charge, smaller volume, and great freedom in shaping the batteries to available space. Though the energy density (KWh/kg) of polymeric batteries are, in current estimation, comparable to that of the lead-acid battery, charging of the batteries, which is the most critical routine operation of a diesel-powered submarine and requires about two hours to complete, can be reduced drastically with the use of polymeric batteries.

Polymer electrolyte membrane fuel cell (PEMFC) technology has been receiving increased attention due to its high energy efficiency and environmentally friendly nature [74,75]. Among the different technologies developed, PEMFCs which operate at temperatures above 150°C have certain advantages that result in better overall performance and simplification of the system. The polymer electrolyte membranes (PEMs) in high-temperature PEMFCs must enable proton conduction and, at the same time, exhibit mechanical, thermal, and oxidative stability under operating conditions. The state-of-art material used in high-temperature PEMFCs is polybenzimidazole (PBI) which can be doped with various strong acids. In the case of phosphoric acid, PBI exhibits high acid uptake, resulting in highly conductive materials [76]. However, PBI has several drawbacks, such as moderate mechanical properties, reduced oxidative stability, limited availability, and high cost.

Among the alternative polymeric structures developed recently for PEMFC application, mention may be made of aromatic polyethers containing polar pyridine units in the main chain [77,78]. Novel poly(aryl ether sulfone) copolymers containing 2,5-biphenylpyridine and tetramethyl biphenyl moieties have been synthesized [78] by polycondensation of 4-fluorophenyl sulfone with 2,5-(4', 4''-dihydroxy biphenyl)-pyridine and tetramethyl biphenyl diol (see Figure 5.38). These polymers exhibit excellent film-forming properties, mechanical integrity, high modulus up to 250°C , high glass transition temperatures ($> 280^\circ\text{C}$) as well as high thermal stability up to 400°C . In addition to the above properties required for PEMFC application, this polymer shows high oxidative stability and acid doping ability, enabling proton conductivity in the range of $10^{-2} \text{ S.cm}^{-1}$ above 130°C [78].

5.5 Polymers in Photoresist Applications

Polymers and polymeric systems that can undergo imagewise light-induced reactions are of great technological importance [79–84]. Photoresists are polymers or polymeric systems (polymer binders containing dispersed or dissolved photoactive compounds) which, applied as a surface coating to an

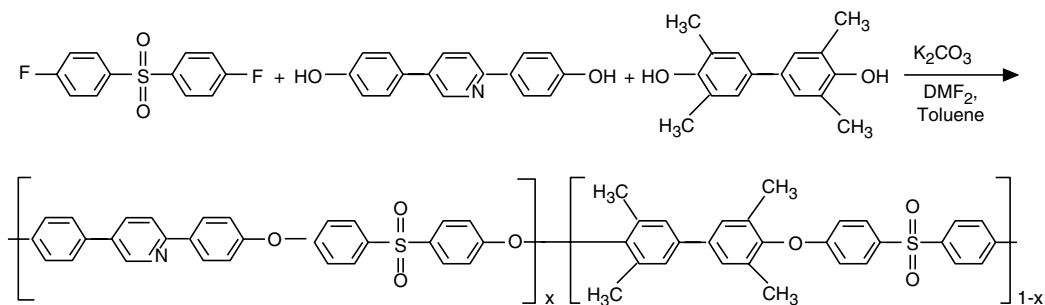


FIGURE 5.38 Polycondensation of 4-fluorophenyl sulfone with 2,5-(4',4'')-dihydroxy biphenyl)-pyridine and tetramethyl biphenyl diol for the preparation of poly(aryl ether sulfone) copolymers containing 2,5-biphenylpyridine and tetramethyl biphenyl moieties. (After Pefkianakis, E. K., Deimede, V., Daletou, M. K., Gourtoup, N., and Kallitsis, J. K. 2005. *Macromol. Rapid Commun.*, 26, 1724. With permission.)

underlying substrate, undergo some type of reaction upon exposure to visible or ultraviolet radiation such that the differences in solubility of the exposed and unexposed areas can be exploited to obtain selective removal of either the exposed or unexposed area of the film (a process known as development). Thus, by providing suitable radiation exposure of the polymer-coated surface through a pattern or mask, such as a negative, an image can be generated on the substrate. The image can then be transferred permanently to the substrate by etching, deposition, etc. Since such images are raised above the substrate on which the polymer has been coated (see Figure 5.39), they are called relief images. In order for the image to be transferred to the substrate, the polymer must “resist” the chemical activity of the particular

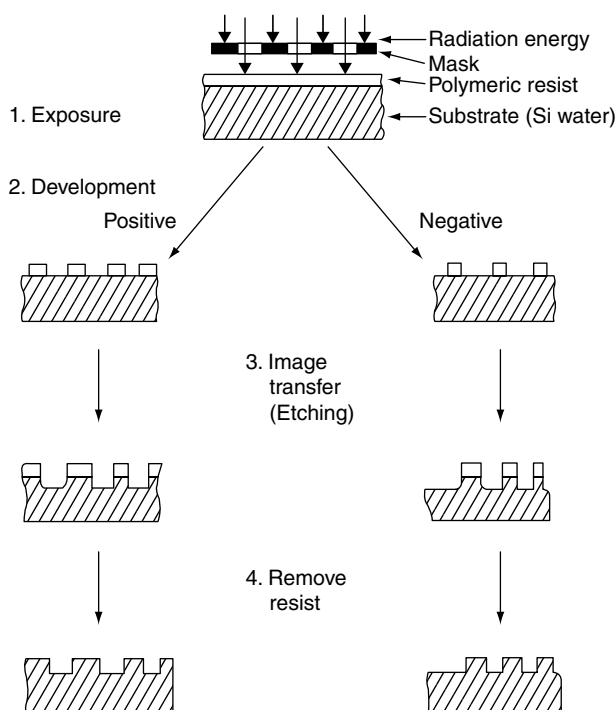


FIGURE 5.39 Positive and negative modes for a photoresist film.

etchant, which can be either a wet (solvent) or dry (plasma) process. Thus, they polymers are called photoresists.

There are a number of types of photoresist that function by a variety of mechanisms, such as:

1. Cross-linking of a linear polymer backbone by the light-induced decomposition of a photosensitizer to generate active species (e.g., cyclized rubber with azide type photosensitizer).
2. Cross-linking of a polymer containing photosensitive groups within its own structure [e.g., poly(vinyl cinnamate)].
3. Polymerization of a monomeric material to yield a reduced solubility polymer (e.g., methylene bisacrylamide monomer and benzoin photoinitiator in polyamide as the carrier polymer).
4. Enhancement of solubility by a photoinduced molecular rearrangement (e.g., naphthoquinone diazide in a novolac binder resin).
5. Enhancement of solubility by reduction in molecular weight by bond scission (e.g., poly(methyl methacrylate) deep-UV resist).
6. Depolymerization by high energy irradiation to allow a kind of ablative imaging (e.g., by irradiation with laser or an electron beam).

Figure 5.39 shows schematically the positive and negative modes of lithographic processes with a photoresist film. When exposure of the photoresist film to radiation produces an image that is less soluble in the developer, a negative image results. Negative images are generally produced by photochemical reactions that lead to crosslinking and network formation in the polymer film in the exposed area. Such network polymers are insoluble in the developer solvent. A second means of generating a negative image is to produce a photoinduced change which makes the exposed areas less soluble in a selective developer.

A positive image results when the areas of the film exposed to radiation are more soluble than the unexposed areas in the developer (Figure 5.39). There are two classes of chemical reactions that can lead to enhanced solubility of the exposed areas. The first is a photochemical change that converts the exposed area to a different polarity as compared to the unexposed areas. A selective dissolution of the exposed areas can then be obtained with the proper choice of a developer. The second chemical change that can occur is a backbone cleavage of the resist polymer such the exposed area of the polymer film is degraded to a low molecular weight (or all the way to monomer) that has a dissolution rate significantly higher than the rate for the unexposed higher-molecular-weight area in the developer.

There are two important aspects of the performance of a photoresist: imaging (lithography) and image transfer (resistance). An image must be formed in the resist polymer and then the image must be transferred permanently into the substrate or to other materials by etching, deposition, etc. The term photolithography is also used to refer to both the processes. Traditionally, photolithography has had great commercial impact on the printing industry, photomachining of fine parts, and so on.

More recently, the revolutions in the field of electronics have been made possible by the photopolymers (microresists) used to delineate the tiny features that make up modern integrated circuits. The microlithographic applications of photopolymers have been the driving force behind most of the technological and scientific activity in the area over the last three decades. Most of the devices that have been manufactured using microlithography have employed one of two resist systems. Negative working resists based on cyclized rubbers and bisazides were the original mainstays of this industry. Although these resists are still in use today, novolac/naphthaquinone-diazide-based positive photoresists are used for most features less than 3 μm in size. The smallest details defined by photolithography in factories are about 2 μm wide.

The drive to smaller features sizes in microlithography has brought in its wake a trend toward shorter wavelengths for the exposure radiation. To a very rough approximation, the resolution limit of an optical exposure source is give by 2λ , where λ is the wavelength. As the wavelength decreases, the potential resolution thus becomes smaller, i.e., better. This, however, requires that are sensitive at these shorter wavelengths and also exposure sources that are capable of sufficient output at these wavelengths.

Almost all commercial exposure sources use super-high-intensity Hg or Hg/Xe lamps with high-intensity outputs at 436, 405, 365, 330, and 313 nm. The first three wavelengths are normally grouped and called the near-UV. The next two wavelengths are called the mid-UV. Radiation from these lamps and other sources with wavelengths below 280 nm comprises the deep-UV. With the development of excimer lasers high-output deep-UV sources have become readily available.

Though the majority of current microlithography for semiconductor processing is carried out using radiation in the near-UV, it is resolution-limited by its relatively long wavelength. The submicron resolution that is required for increasing sophistication and degree of integration is more readily achievable by going to shorter wavelengths, and there is currently much interest in using not only deep-UV but also x-rays, ion beams, and electron beams for exposing resist. Each of these technologies has specific resist requirements, and various polymeric resist systems have been developed and are under development.

The other change in resist processing involves the use of multilayer schemes in place of a simple photoresist coating. Microimaging using multilayer materials and technology has revolutionized the electronics industry. Many silicon chips used in calculators and computers are produced in some variation of the following sequence of operations:

A silicon wafer that has one surface oxidized to a controlled depth is coated (on the oxide surface) with a photoresist, such as poly(vinyl cinnamate), to produce a thin and uniform coating several micrometers thick when dry. Exposure to UV light through a mask insolubilizes part of the polymer. The uncross-linked polymer is washed off solvents. The bare substrate parts that thus reappear are etched through the oxide layer down to the silicon layer by a fluoride solution in water or by a plasma that contains reactive ions.

Operations are then performed to alter the chemical composition of the etched regions. The operations may include ion implantation to introduce dopants that make semiconductors of the diffused-base transistor type and depositing a layer of aluminum to act as a conductor or a layer of other materials to act as insulators. After removing all of the remaining polymer by solvents, plasmas, or baking, the wafer is recoated and a new pattern is imposed and processed. The sequence may be repeated as needed to produce integrated circuits with many such layers and with amazing complexity. The minimum line widths on chips produced by photolithography are usually in the 5- μm range. However, to produce large-scale integrated circuit (LSI) devices, minimum line widths must be decreased to pack more circuits on a chip.

5.5.1 Negative Photoresists

Most negative-working resist systems are based on the fact that the dissolution rate of a polymer decreases as the molecular weight increases, and the polymer ultimately becomes insoluble in any solvent as a crosslinked network is formed.

A system widely used in silkscreen printing takes advantage of the photosensitization reaction of the dichromate/poly(vinyl alcohol) or dichromate/gelatin system. The mechanism of these dichromate resists is obscure, but it is thought that the formation of the chromate ion from the dichromate ion is an important initial step:



This is followed by the transition of chromium from Cr(VI) to a low state of oxidation, and an interaction process with the hydrophilic polymer to form a chromium/polymer complex in which binding between the polymer and photoreleased chromium compound involves either primary forces or physical forces of absorption. The resulting complex causes a solubility decrease in the aqueous system used for development.

The dichromate resists as also the diazo resist systems developed later suffer from limited stability and limited exposure wavelength sensitivity and are very slow photographically. These have therefore been

displaced for resist applications by better-characterized negative photoresists using photodimerization (cinnamate type resist), photocrosslinking (bisazide resists), and photoinitiated polymerization (free-radical or cationic) to yield insoluble polymer networks.

The simplest photodimerizable resist is poly(vinyl cinnamate), made by esterification of poly(vinyl alcohol) with cinnmoyl chloride. Upon exposure, the cinnamate groups can dimerize to yield truxillate or truxinate. If the two cinnamate groups involved in this reaction are from two chains, the cyclic product represents a cross-link (Figure 5.40).

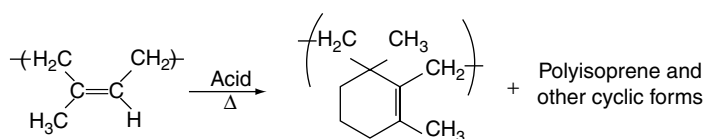
There are many cinnamate resins, including derivatives of poly(vinyl alcohol), cellulose, starch, and epoxy resins. It is the epoxy resins that have found the most applications in lithographic materials.

As cinnamate resins are water-insoluble, a suitable solvent, such as trichloroethylene, is used to achieve the solubility differential for image development. An emulsion of the solvent dispersed in an aqueous phase of gum arabic and phosphoric acid is generally used. The light-exposed regions of the coating are rendered insoluble due to cross-linking and form the printing image.

Poly(vinyl cinnamate) itself is only weakly absorbent above 320 nm. Its photoresponse is generally of the order of a tenth of that of dichromated colloids, but the rate can be accelerated by the use of photosensitizers, such as nitroamines (increase of the order of 100 times), quinones (increase of the order of 200 times for specific ones), and aromatic amino ketones (increase of the order of 300 times for specific ones). A commonly used aromatic ketone is 4,4'-bis(dimethylamino)-benzophenone, also known as Michler's ketone.

The Kodak photoresist based upon the poly(vinyl cinnamate) system is particularly suitable for printed circuit manufacture. It also finds application in some invert halftone photogravure processes and photolithographic plates. The property of superior adhesion to metal of cinnamic esters of particular epoxy resins has resulted in the preferred use of these resins for platemaking. Very few of the cinnamate-type resists have, however, been used in micro applications.

A negative-working resist system that has seen extensive use in microlithography and continues to be used where high resolution is not required, is that based on the photochemistry of bisazide as the photoactive compound in a cyclized or partially cyclized polyisoprene rubber as the binder resin. Since poly(*cis*-isoprene) has a low glass-transition temperature and is too soft for use in lithography, partial cyclization is performed to yield a polymer with good adhesion and film forming properties. The cyclization of polyisoprene catalyzed by acid produces a complex mixture of structures that increase the T_g of the rubber while reducing the solution viscosity so that high solids coatings are possible:



The partially cyclized rubber also has improved film-forming properties.

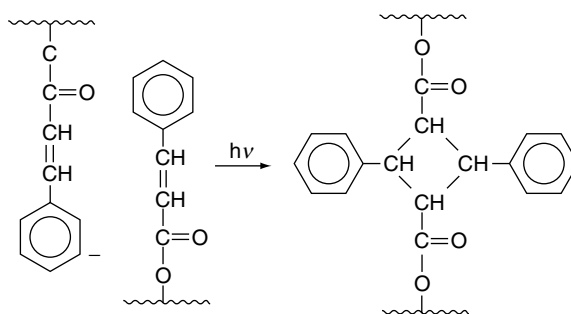


FIGURE 5.40 Photodimerization of poly(vinyl cinnamate).

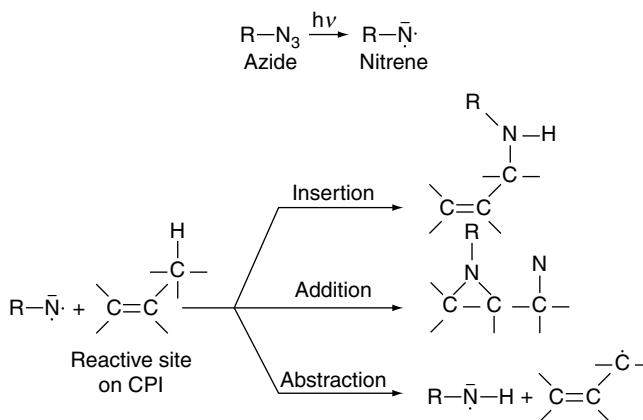


FIGURE 5.41 Reaction of nitrene formed by photodecomposition of azide, with cyclized polyisoprene (CPI) polymer.

The azide-type photoactive compounds used with the above type of resist have good thermal stability and decompose efficiently upon UV irradiation from mercury lamps to give intermediates known as nitrenes. The nitrenes being highly reactive undergo several reactions, e.g., (1) insertion reactions with carbon-hydrogen double bonds to yield secondary amines, (2) addition reactions with carbon-carbon double bonds to produce aziridines, and (3) abstraction reactions that generate radicals. These chemistries are shown in Figure 5.41. When a bisazide is used, a bisnitrene is formed on irradiation which then cross-links the polyisoprene by reacting with the double bonds or the allylic hydrogens in the exposed regions to produce an insoluble matrix (see Figure 5.42). Resists that use bisazides are mostly near UV (436 nm) resists.

The drawback of the bisazide-based cyclized rubber resist becomes manifest during development. A good solvent must be used to remove the unexposed high polymer. However, this solvent also penetrates and swells the images that are to be left behind. Though with large ($> 10\ \mu\text{m}$) spaces between images, the image returns to its original position, with small ($< 3\ \mu\text{m}$) spaces, two neighboring images may swell,

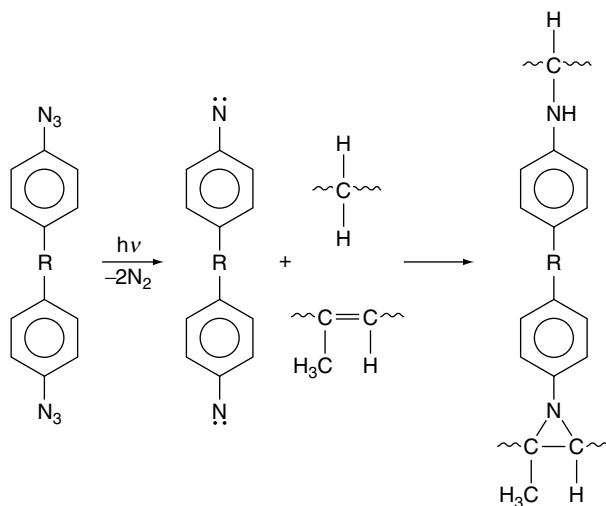


FIGURE 5.42 Cross-linking of polyisoprene by irradiation of a mixture of polyisoprene and a bisazide.

touch, and coalesce to leave a polymeric bridge between the two images. Such a bridge will finally translate into a short in the electronic circuit.

A novel microlithographic application for photoinitiated polymerization involves the polymerization of a monomer and the locking-in of a plasma-sensitive host polymer so that plasma techniques can be used to carry out all-dry development, thus avoiding the problems of swelling and resolution limitation associated with standard resists. Some plasma-developable resists are described later in this section.

5.5.2 Positive Photoresists

Positive photoresists have been increasingly important because of their higher resolution capability and better thermal stability. They become more soluble in exposed areas by increasing their acidity or by undergoing bond scission and degradation of polymer chains.

5.5.2.1 Near-UV Application

At near-UV wavelengths it is not possible to enhance solubility by photoinduced bond scission because the light is not energetic enough, and consequently an alternative mechanism is used. Positive resists with

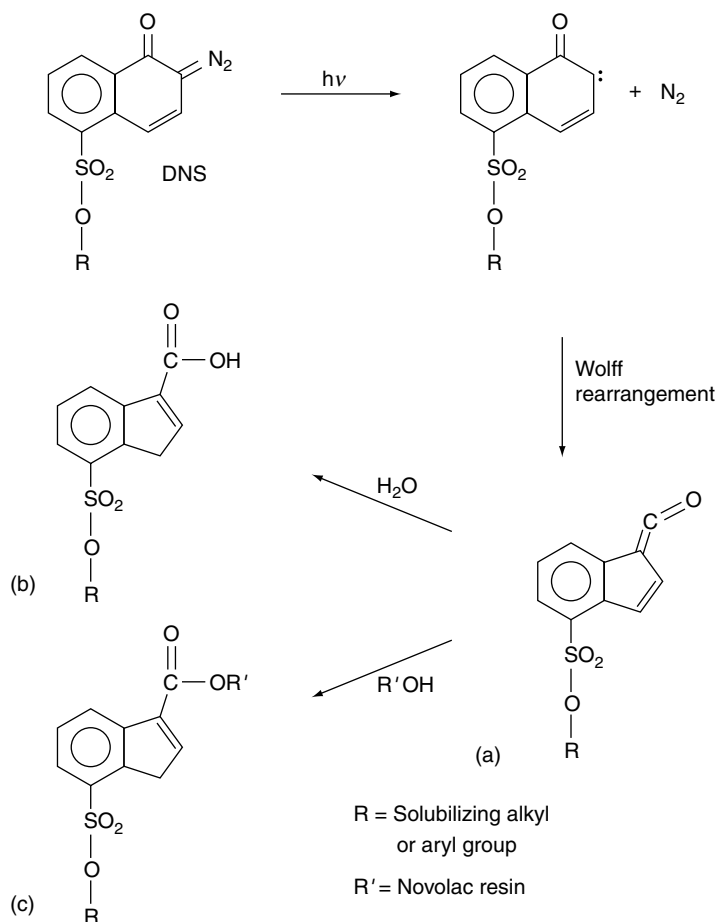


FIGURE 5.43 Photolysis of diazonaphthoquinone sulfonate esters (DNS) followed by (a) Wolff rearrangement to a ketene intermediate, which (b) reacts with water to form an indene carboxylic acid or (c) reacts with phenolic hydroxyl groups (in absence of water) to form ester linkages.

sensitivity in the near-UV usually comprise a large photoactive molecule that is insoluble in basic solvents and also sufficiently bulky to inhibit dissolution of a base soluble polymer. On exposure, the photoactive compound breaks down to form a base-soluble product and the exposed region can then be washed out using a basic solvent. The base soluble polymeric binder is typically a novolac resin of relatively low molecular weight.

The most commonly used photoresists for resolving features of 5 μm and below are based on the photolysis of diazonaphthoquinone sulfonate esters (DNS), which are used as the photo-sensitive compound in a novolac binder resin. Upon exposure at near-UV wavelengths, the photosensitive compound undergoes a Wolf rearrangement. Nitrogen is given off in this reaction producing a ketene intermediate (Figure 5.43a), which reacts with water in the film to form an indene carboxylic acid (Figure 5.43b). Under normal ambient working conditions, enough water is present in the novolac binder to ensure the formation of the carboxylic acid. However, in the absence of water, the ketene intermediate has been shown to react with the phenolic hydroxyl groups on the novolac to form pendant ester linkages (Figure 5.43c).

The unexposed DNS in the masked areas acts as a dissolution inhibitor for the novolac binder, presumably due to its hydrophobic nature, while the indene carboxylic acid that is formed from the photolysis reaction in the exposed areas is a dissolution accelerator for the novolac. The rate of development in an aqueous base is much higher for the exposed areas, which promotes good developer discrimination between the exposed and unexposed areas leading to high-contrast, high-resolution images. It has been proposed, however, that this simplistic picture of hydrophobic-to-hydrophilic switch may not represent all of the factors that enable the high discrimination and high contrast obtainable in this type of resists. The enhancement in dissolution rate may also be a result of the gaseous nitrogen that is formed during the DNS photolysis (see Figure 5.43). It is hypothesized that the nitrogen evolution causes microvoids and stresses in the novolac film and that this promotes the diffusion of the developer into the polymer film leading to an increase in the dissolution rate.

Novolacs produced by cresol-formaldehyde condensation have been the polymers of choice for the DNS photochemistry. These novolac resins are usually synthesized from commercial cresol mixtures, which contain about 60% *m*-cresol, 30% *p*-cresol and 10% of various other aromatic phenols.

These polymers are soluble in spin-coating solvents, show good film-forming and coating properties, provide excellent adhesion to most substrates, and exhibit enough balance in the needed binder properties to be used almost exclusively in all commercial DNS containing positive photoresist formulations.

With the increase in demands on photoresist formulations due to smaller imagery and new image transfer steps, such as ion implantation and plasma etching, novolacs are, however, found to fall short in two areas. First, a specific chemical composition and molecular size is difficult to reproduce because the exact composition of the cresol starting materials can vary from lot to lot and because the condensation polymerization of the cresol with formaldehyde is difficult to control, which results in a relatively low-molecular-weight polymer with M_n around 1000 and with a broad dispersity (about 20–40). These variations can lead to irreproducible lithographic performance of the high-resolution resists. Second, novolacs have low glass transition temperatures (T_g), generally in the range of 20–120°C depending on molecular weight, which often lead to unacceptable image distortions when the image is subjected to plasma etching or ion implantation process steps.

For several years, many of the commercial positive photoresists have contained multifunctional, principally trifunctional, DNS derivatives, some examples of which are shown in Figure 5.44. They contribute to enhanced image stability during the image transfer step in addition to higher contrast and faster development in the microlithographic process.

As stated earlier, the developer used to dissolve or develop out the exposed regions of the DNS-based positive photoresist coatings is an aqueous base. There are two general types of these aqueous-base developers. The first type, the metal-ion containing developers, is based on metallic hydroxides. The need to eliminate metal ion contaminants in semiconductor processing has led to the development of a second category of metal-ion free developers. The most important members in this category are quaternary

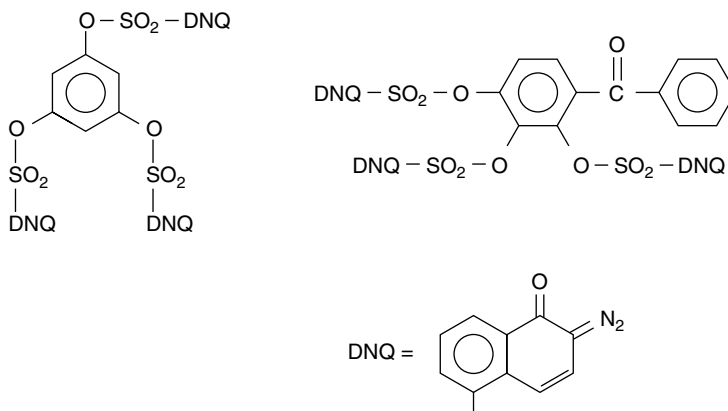


FIGURE 5.44 Typical examples of multifunctional diazonaphthoquinone sulfonate esters used in photoresists.

alkylammonium hydroxides, such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, etc., used in aqueous solutions.

The DNS/novolac-based positive photoresist can also be used to obtain negative images by an image reversal process involving post-exposure treatment of the photoresist film with a reactive amine. This amine-treated film is heated and then flood-exposed. Development with a conventional aqueous base at this stage produces a high resolution negative image of the original positive image. This process is shown in Figure 5.45. An amine (e.g., monazoline, imidazole, triethanolamine) reacts with the indene carboxylic acid in the originally exposed areas to form an ammonium salt that decomposes on heat treatment to indene. Subsequent flood exposure gives indene carboxylic acid in the previously unexposed areas that are then washed out in the aqueous base developer. The hydrocarbon indene from the original exposure and subsequent process protects the novolac just as the original DNS would do.

5.5.2.2 Mid- and Deep-UV Photoresists

Though conventional positive resists have performed well at 436, 405, and 365 nm wavelength (common outputs of commercial exposure sources), the potential resolution gain has been small. This has given a push toward shorter wavelengths for achieving higher resolution.

A DNS-based positive photoresist can be used for deep-UV exposures if the binder resin in the photoresist itself does not absorb. Since novolacs made from the condensation of formaldehyde with pure *p*-cresol (instead of commercial cresol mixtures) are found to have very transparent windows at about 250 nm, a DNS/*p*-cresol novolac-based photoresist gives a positive image after deep-UV exposure and development with aqueous base. A copolymer of styrene and maleimide is also used in place of novolac as a binder for DNS-based deep-UV positive resists.

The photochemistry of *o*-nitrobenzyl esters (Figure 5.46) has been used as the basis for another dissolution inhibitor approach to making deep-UV resists. In this case, the polymer binders are base-soluble copolymers containing methacrylic acid and the dissolution inhibitor is an *o*-nitrobenzyl ester of a large organic molecule such as cholic acid. The ester cleaves, upon exposure, to form products (Figure 5.46) that no longer interfere with the resin dissolution, and thus a positive relief image is obtained after development.

Deep-UV resists are used in two principal modes: as surface resist in single layer mode, or as the thick planarizing layer in portable conformable mask (PCM) bilayer mode. In the single layer mode, the use of deep-UV resists provides improved resolution, while in the PCM mode, a deep-UV resist is used in combination with a conventional resist to make use of the wavelength selectivity of the two types of resists. The PCM process (Figure 5.47) first exposes and develops the conventional novolac-based thin top resist using a 436 nm masked exposure. A second full exposure is then made in the deep-UV, which is

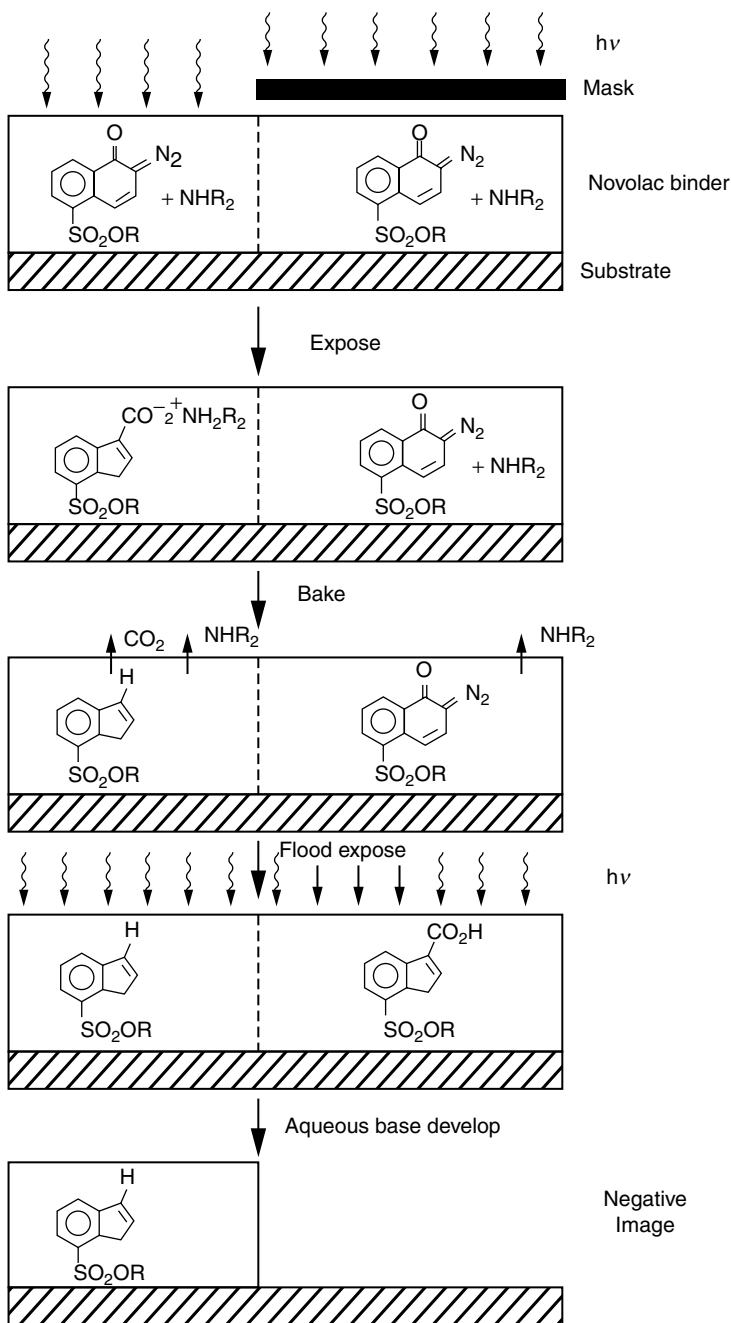


FIGURE 5.45 Schematic of image reversal process of DNS-novolac positive photoresist.

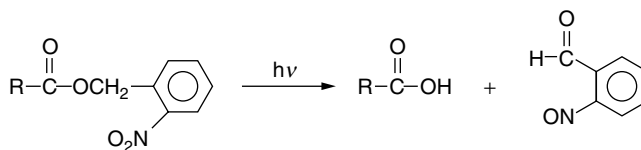


FIGURE 5.46 Photochemistry of *o*-nitrobenzyl ester.

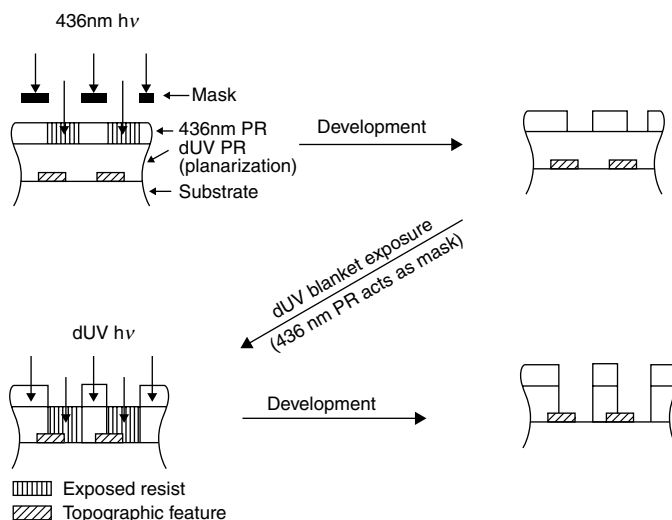


FIGURE 5.47 Schematic of portable conformable mask (PCM) bilayer process. (PR, photoresist; dUV, deep-UV).

masked by the novolac-based resist image of the 436 nm exposure. The unmasked (exposed) positive-working deep-UV resist is developed to give a thick, high-resolution image for subsequent processing.

The use of a photolabile acid generator to deprotect imagewise a functional group or depolymerize a polymer is the best-documented example of photochemical change systems that are known to proceed by a chain reaction mechanism. A new term, chemical amplification, has been coined to describe any of several such systems. Many photolabile acid generators are possible, but the most widely used have been iodonium and sulfonium salts, which have their natural sensitivity between 200 and 300 nm but can be substituted and sensitized out into the visible.

Polymers with acid-labile protecting group such as *t*-butyl carbonate and *t*-butyl esters have been doped with iodonium and sulfonium salts, which produce acid on radiation exposure in resist matrix. Imagewise exposure of these resist formulations to generate acid and then heating produces a relief image (Figure 5.48a). Either positive or negative images may be developed depending on the solvent chosen.

The design and synthesis of polymers with carbonate units in the backbone that allow a facile degradation of the polymer by the chemical amplification scheme with photoacid have been reported. The exposed areas of such resists can be developed by a solvent giving high-resolution positive images. On the other hand, polymers containing precursors to more volatile fragments such as copolycarbonate (Figure 5.48b) may be dry developed by thermal treatment alone. Thus, after exposure of the copolycarbonate in the presence of a photoacid and thermal treatment of 60°C for 2 min, complete image cleanout was observed.

Polymers capable of facile depolymerization upon irradiation may be suitable as “self-developing” positive resists. One polymer where depolymerization has been successful is polyphthalaldehyde (Figure 5.48c). End-capped polyphthalaldehyde is stable to a temperature of 150°C, although its ceiling temperature is -40°C . When polyphthalaldehyde is irradiated with a high-powered excimer laser, it is blown away as monomer during the exposure. This type of ablative imaging is possible because of the high-energy output of the laser. Moreover, in the presence of an onium salt, the depolymerization can be catalyzed imagewise.

The excimer laser mentioned above filled a long-standing need for a workable exposure source for deep-UV lithography. The excimer laser can deliver large amounts of light at several deep-UV wavelengths, depending on the mixture in the laser gas chamber. Several of the possible outputs of this tunable tool according to the excited complex that emits light are listed in Table 5.13.

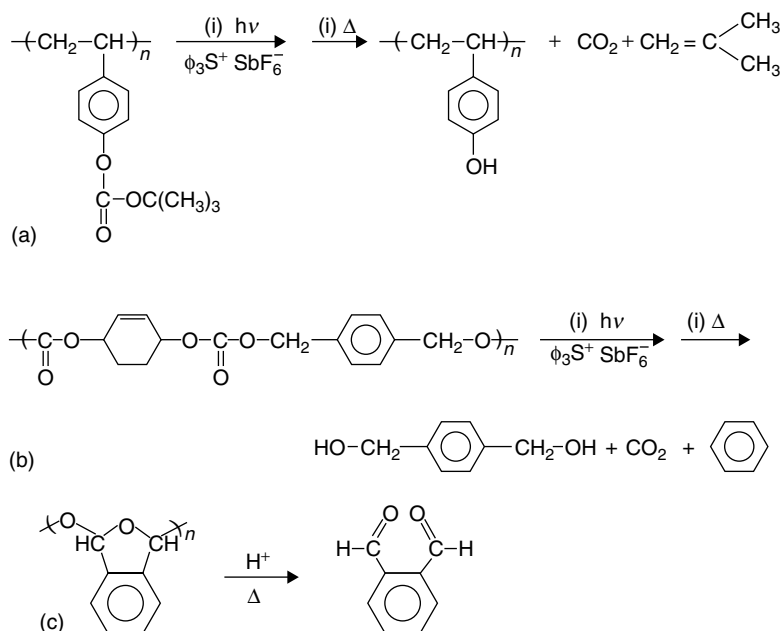


FIGURE 5.48 Photochemistry of poly(4-*t*-butoxycarbonyloxy styrene) doped with (a) triphenylsulfonium hexafluoroantimonate, (b) a dry developable polycarbonate, and (c) self-developing polyphthalaldehyde.

The extremely high-energy output of the laser also allows the potential of the above kind of ablative imaging with other polymers. For example, when PMMA is used with an ArF (193 nm) laser, the exposure produces a large amount of scissioning in the top surface. The fragments are blown out of the exposed hole by the kinetic energy of the photopulse, while continued pulses drill through the resist. Generally, the energy output is so great that almost any polymer can be ablated.

5.5.3 Electron Beam Resists

With the demand for greater and greater device integration, as in the technology of random access memories where the number of devices to be accommodated on a piece of silicon has increased dramatically with no concomitant increase in the device area, the geometry of the features on a chip has continued to fall and routine production is now in the submicron range for some advanced devices. Imaging such small geometries call for new lithographic processes. One of the most important of these new processes uses an electron beam to irradiate the resist and is known as electron beam lithography. Focused beams of electrons or focused ion beams are the fundamental methods of generating patterns with dimensions far into the submicron range.

TABLE 5.13 Excimer Laser Outputs

Complex	Wavelength (nm)
Ar-F	193
KrCl	222
KrF	248
XeBr	282
XeCl	308
XeF	351

An electron beam is of much shorter wavelength than the radiation used in standard microlithography and, therefore, provides greater resolution possibilities. For resist exposure a beam of electrons can be used whose position is controlled by a computer-driven beam deflector, thus obviating the need for a mask. Both positive- and negative-working resists are used for electron beam lithography.

Since an electron beam having shorter wavelength and higher energy can cause covalent bond scission relatively easily, polymer degradation by exposure to the beam forms the basis for a positive photoresist system. Poly(methyl methacrylate) and its analogues, such as poly(hexafluorobutyl methacrylate), have been widely studied as positive-working electron resists. Exposure to an electron beam causes extensive main chain scission in these polymers, but depolymerization back to monomer does not occur. Moreover, PMMA is not very sensitive and so other materials have been employed. Polyolefin sulfones, for example, are extremely sensitive positive-working electron resists, undergoing chain scission back to the olefin and SO₂.

Polymers containing reactive cross-linking groups such as epoxy or allyl are commonly used for negative-working electron beam resists. A typical example is a copolymer of glycidyl methacrylate and ethyl acrylate. Co-polymers of glycidyl methacrylate and 3-chlorostyrene have been shown to have high sensitivity, good adhesion, and plasma resistance. These materials are commercially available.

One drawback in electron beam lithography arises from the fact that much of the interaction between the polymer and the electron beam occurs as a result of low-energy secondary electrons being produced in the film. These are scattered beyond the definition of the exposing beam and produce unwanted reactions in areas adjacent to the primary exposure. This effect, known as the proximity effect, can cause undercutting and merging of closely spaced features. However, in x-ray and ion-beam lithography, the secondary electrons produced have lower energies and shorter path lengths, and consequently the proximity effect is less pronounced. X-ray and ion-sensitive resists may thus find greater use in the future.

5.5.4 Plasma-Developable Photoresists

One important area of resist research in recent years is the development of plasma-developable resist systems. The aim of plasma developable resists is to use nonsolvent, all dry development methods to avoid the problems of swelling and consequent resolution limitation associated with conventional resists. Much of the semiconductor fabrication process now utilizes plasma techniques as they are capable of providing high resolution images. An important consideration in this is that the plasma-developable resist images should stand up well to the plasma etching treatments.

Plasma resistance of organic polymers can increase significantly due to the presence of aromatic and heteroatomic groups. So if a resist could be made such that after exposure, the exposed area contained more of these groups than the unexposed area a differential plasma etch rate would be achieved leading to selective development (Figure 5.49).

A process known as *photolocking* based on the above method was developed at Bell Laboratories. The process used a resist consisting of a plasma degradable acrylic polymer such as poly(dichloropropylacrylates) intimately mixed with a readily polymerizable volatile monomer such as *N*-vinyl carbazole or acenaphthylene. Upon exposure to UV radiation through a mask, the monomer only in the exposed areas polymerizes and becomes locked in the plasma sensitive host polymer. After exposure, the monomer in the unexposed regions is removed by application of vacuum leaving the plasma-sensitive poly(dichloropropylacrylate), while in the exposed regions the photolocked polymers of *N*-vinyl carbazole or acenaphthylene provides plasma resistance, thus facilitating selective development. This type of photolocking system is particularly suitable for x-ray lithography.

In photolocking systems, *N*-vinyl carbazole, which is rather toxic, was subsequently replaced by a number of silicon containing monomers. A novel feature of such silicon-based monomers (XI) is that, on oxygen plasma treatment for final resist removal, they deposit a thin layer of silicon dioxide, which is itself a useful protective dielectric layer.

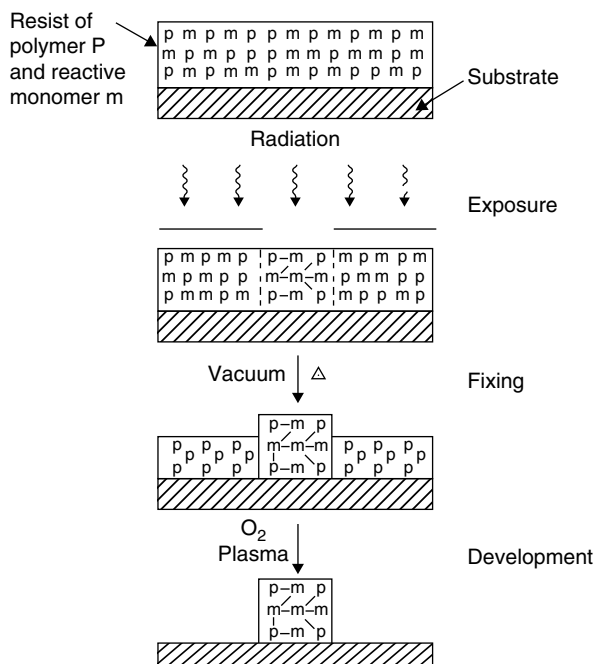
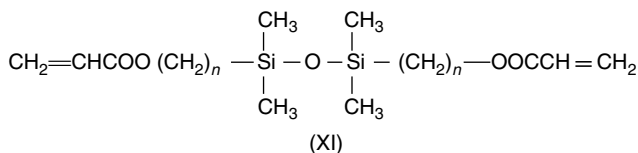


FIGURE 5.49 Schematic of photolocking process used to bind etch-resistant molecules imagewise in a polymer film.



5.6 Photoresist Applications for Printing

Photoresists find applications in several of the printing processes. The major areas of interest include printing plates, photoengraving, silkscreen printing, printed circuits, collotype, and proofing systems.

5.6.1 Printing Plates

Photopolymerization by actinic radiation is used extensively in the preparation of printing plates. The kind of plates may be categorized into three groups: (1) relief or raised image; (2) planographic, photolithography; and (3) gravure or intaglio-photogravure. Photopolymerization, however, finds use primarily in (1) and (2).

5.6.1.1 Relief or Raised-Image Plates

The traditional copper, zinc, and magnesium plates used by the bulk of letterpress printers and platemakers are now being replaced by photopolymer platemaking, because the latter is a more rapid and simpler process, and permits faster processing. Photopolymer plates can be made accurate to the negative. The principle of relief plate making is depicted in Figure 5.50. Press life for photopolymer plate systems is satisfactory, generally up to about half a million impressions, though current systems claim longer.

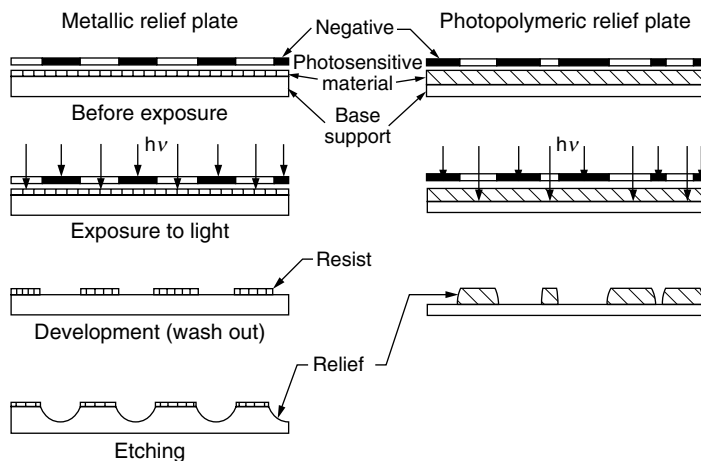
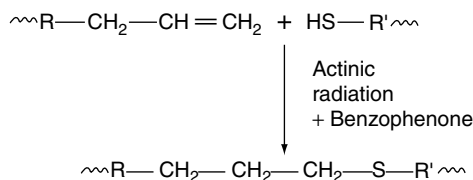


FIGURE 5.50 Principle of relief plate making.

Photosetting in conjunction with photopolymer plates has a vast potential in three chief areas of printing, namely, newspaper production, flatbed cylinder letterpress, and rotary letterpress commercial printing.

Photopolymer relief plates fall into two principal categories: liquid types and solid types. Presensitized liquid and dry raised-image or relief plates are used for letterpress, dry offset, and flexography.

The first liquid photopolymer system was the letterflex plate. The process relies on the cross-linking reaction of a polyurethane possessing allylic unsaturation and a polythiol, i.e.,



The liquid photosensitive resin is employed as a top coating on an aluminum support. A negative is then used and exposed to actinic radiation from a Xenon lamp. The unexposed areas are removed with a solution of surface-active agents using an ultrasonic washing technique.

Solid photopolymer plates for printing were pioneered by Dupont with the introduction of Dycril in 1957. The photosensitive layer in Dycril is a 0.3–1.0 mm thick binder composed of a water-soluble cellulose derivative such as cellulose acetate succinate, a monomer of the divinyl type such as triethylene glycol diacrylate, and a photo-initiator such as 2-ethylanthraquinone and a thermal stabilizer (inhibitor) of the *p*-methoxyphenol type. The mixture is applied on an aluminum support or steel with an adhesive sheet and exposure to actinic radiation from a carbon or mercury arc lamp is performed through a negative placed over the photosensitive layer. Postexposure treatment involves washing with a 0.2–0.5% caustic soda solution that removes the unexposed area and leaves a relief on the support. Dycril is fairly cheap, has a fairly high resolving power, and is durable.

Nyloprint, of BASF is a solid type of photosensitizer compound coated plate, around 1967. The solid photopolymerizing material is a combination of an alcohol-soluble polyamide (such as a polyamide copolymer of hexamethylene diammonium adipate and ϵ -caprolactam), a vinyl monomer (such as bis-acrylamide, hexamethylene bis-acrylamide, triethylene glycol diacrylate, etc.), a photo-initiator such as benzoin methyl ether, and an inhibitor (such as hydroquinone) and maleic anhydride to function as a

compatibilizer for polyamide with vinyl monomers. Post-exposure treatment of Nyloprint, however, involves washing with alcohol.

Dyna-flex, a solid photosensitive plate marketed by Dynaflex, has a photosensitive emulsion on an aluminum backing or carrier plate and is thought to be based on poly(vinyl alcohol) and dichromate chemistry.

5.6.1.2 Photolithography/Planographic Plates

These are lithographic plates and find application on offset presses. The photosensitive materials used include diazo monomers, diazo polymers, and diazo compounds, in conjunction with additive film formers such as epoxy resins, phenolics, poly(vinyl acetals), polyamides, azide compounds, unsaturated chalcone, cinnamate, stilbene, and vinyl polymers and dichromated colloids. Three kinds of metallic photolithographic plates are used. These are surface plates, deep-etch plates, and bimetallic or trimetallic plates.

Surface plates are either negative- or positive-working and direct use is made of the coating material or the resultant compounds of photochemical change as the image bearer. The other two types of plates may be regarded as “reversal” positive working processes in which the coating acts as a hydrophilic stencil, and the image is in essence composed of the plate surface backed up by the lacquer application.

Deep-etch plates and trimetallic plates require a positive transparency for their preparation, whereas bimetallic plates are generally processed from photographic negatives. A bimetallic plate has an oleophilic metal, such as copper or zinc, in the image area and another one, such as chromium or iron, in the non-image areas. For trimetallic plates, backing occurs from a third metal for support. Etching is done with ferric nitrate solution, which dissolves the copper but does not attack the metal underneath. The photoresist is removed subsequent to etching, the plate is then inked, and desensitization of the nonimage areas is carried out.

Commercial presensitized plates are formulated on two chief groups of photoresponsive compounds, namely, (1) diazo resins and diazo oxides, and (2) cinnamate resins, some of which have been previously described.

5.6.1.3 Photogravure

In photogravure, ink is transferred from recesses in a metal plate or cylinder to the surface to be printed on. In contrast to the halftone processes (see below), depth of color variations are produced by varying the depth of the recesses and, consequently, the ink quantity transferred to the printed surface.

Gelatin or poly(vinyl alcohol)/dichromate photoresist may be used to sensitize the paper on which a mesh-like pattern or hardened gelatin enclosing small squares of unhardened gelatin (corresponding to the cells that will finally constitute the printing areas) is created by exposure underneath a screen made of two sets of transparent parallel lines arranged orthogonally. A positive transparency is then used to expose the paper so that every square is hardened to a depth dependent on the incident actinic radiation intensity. The paper is then transferred to a copper plate or cylinder with the metal against the gelatin. The backing paper is then removed and the image is developed by washing with water to remove the unhardened gelatin. A photoresist image remains, consisting of squares of varying depths partitioned by walls of completely hardened gelatin.

Ferric chloride is used as the etching agent to prevent gas production, as this might dislodge the resist. The greatest depth of etch occurs in the least hardened areas and, conversely, the least depth in the most hardened areas, thus producing shadow and highlight regions. The resist remaining is removed prior to printing.

5.6.2 Photoengraving

Photoengraving is the process by which blocks for illustrations are made. The illustrative material uses either line drawings with lines of differing thickness representing various tones or photographs reproduced as halftone blocks. For halftone work, the continuous tones of the original photographs

are transformed to a uniform pattern of varying sized dots by either a crossline screen placed a short distance in front of the negative or a contact screen placed in contact with the negative prior to exposure.

Clean copper, zinc, or magnesium plates are used, with the fresh photosensitive coating applied over the surface such that on drying it is about 1–4 μm thick. The plate is put under a negative in a vacuum printing frame and exposed to actinic radiation from a carbon arc lamp. After exposure, the plate is washed in running water and the unexposed film areas removed with cotton-wool. The plate is electrolytically or chemically etched after coating the reverse side of the plate with an acid-resistant lacquer such as an alcoholic shellac solution. Zinc or magnesium plates are chemically etched with dilute nitric acid, whereas copper plates are etched with ferric chloride solution. Electrolytic etching is often carried out with copper plates, where they are rendered as the anode in a cell with an iron cathode. A solution of ammonium and sodium chloride is used as an electrolyte. In both types of etching, it is necessary to prevent undercutting of the lines and dots by lateral etching.

5.6.3 Printed Circuits

The use of printed circuits reduces significantly the time necessary to wire electronic apparatus. The design of the circuit ensures that contacts between the components may be provided by a metal coating on an insulating base that is covered with a thin copper layer. Poly(vinyl alcohol)/dichromate or any usable photosensitive system is applied to the copper. The resist is hardened, and the copper regions not forming part of the circuit are removed by etching with aqueous ferric chloride or peroxodisulfate solution.

5.6.4 Collotype and Proofing Systems

Collotype is similar to photolithography as the image areas are made by photocuring dichromated gelatin, with the exception that it has a nonplanar printing surface that is covered with microscopic reticulations. The use of halftones is dispensed with in collotype printing, and the process approaches continuous tone production more closely than any of the other printing methods.

With the advent of proofing systems, photoresist technology allows the graphic arts industry to approximate final full-color print. Photoresist coatings on polyester clear film in the three primary colors, yellow, magenta, and cyan and also in black, can be contacted with color-separation negatives. After exposure, these plastic-supported resists are developed in a manner similar to offset plates and, on superimposition on each other in close registration, afford a good approximation to the final full-color work.

5.7 Optical Information Storage

Optical memory may be defined as any information storage device in which writing and reading of the elements of stored information (pixels) are performed by use of electromagnetic radiation in the visible, infrared, or ultraviolet parts of the spectrum. The case for the use of optical memories in electronic systems rests on general advantages of optical storage systems which are (1) large information capacity (an optical disc, for example, might store 25,000 pages of compressed binary black and white images); (2) high resolution with multivalued pixels; (3) high degree of parallelism and megapixel arrays; (4) high speed resulting from large bandwidth \times channels product and fast optical processes; and (5) no interference of incoherent beams and no EMI.

Polymeric materials can be used for optical information storage and some are ideally suited for the manufacture of optical video and digital audio discs. The information is normally transferred to the polymer using a monochromatic laser by one of four possible methods: (1) pitting of thin films (ablation, hole burning); (2) bubbling of thin films; (3) texture change in liquid crystal film; and (4) bilayer alloying. Of these, technique (1) is of greatest commercial interest. The information is stored by creating, on the polymer surface, a series of small pits that have different lengths and frequency of spacing.

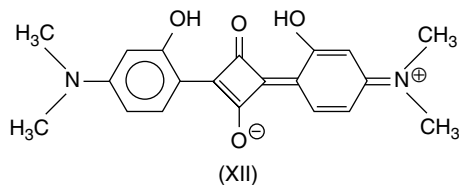
The information can be retrieved by measuring the intensity and modulation of laser reflected from the pattern of pits on the disc surface.

The discs themselves must be fabricated from materials that have the following characteristics: (1) dimensional stability; (2) optical clarity; (3) isotropic expansion; and (4) low birefringence (see [Chapter 3](#)). In addition, the surface should be free of contaminating particles and occlusions that would interfere with the information retrieval process.

The structures that have evolved for ablative-mode optical discs make use of interference effects to minimize the reflectance (R) of the disc in the absence of a hole. A typical ablative-mode optical disc has the structure shown in [Figure 5.51](#). The substrate is an optically transparent material such as polycarbonate, poly(methyl methacrylate), poly(ethylene terephthalate), or poly(vinyl chloride), topped by a subbing layer to provide an optically smooth (to within a fraction of a nanometer) surface for the recording layer. A metal reflector (typically aluminum) is then incorporated next to a transparent dielectric medium such as spin-coated poly(α -methyl styrene) or plasma-polymerized fluoropolymers. This dielectric spacing layer serves both to satisfy the quarter-wave ($\lambda/4$) antireflection conditions and to insulate thermally the A1 reflector from the top absorbing layer where the information pits are created.

A verity of materials have been considered for the absorbing layer in ablative-mode optical discs. Metal/polymer composites offer greater flexibility in optimizing the desired combination of parameters since the functions of energy absorption and ablation can be separated, with the metal absorbing and the polymer ablating. For example, in the proprietary material Drexon, silver particles (formed from silver halide) are dispersed in gelatin. The gelatin matrix ablates at 200°C. It is claimed that the dehydration accompanying ablation means that there is no buildup of material at the edges of the pit ([Figure 5.51](#)), and consequently a higher signal-to-noise ratio, since the buildup of material on the rim of the pit is a factor generating noise.

Dye molecules are an obvious alternative energy absorber, and, like metals, may be used either as thin films or in a polymer matrix. For example, squaryllium dyes (e.g., $R = \text{CH}_3$, $R' = \text{OH}$; XII) may be used as IR absorbers with GaAs or AlGaAs lasers.



The absorbing layer is then protected by a transparent overcoating of crosslinked poly(dimethyl siloxane) elastomer. This will produce a direct read after write, or DRAW, disc that is non-erasable.

5.8 Polymers in Adhesives

An adhesive is a substance capable of holding materials together by surface attachment or adhesive bonding which has many advantages to offer as compared to any other method of attachment [85–88]. When all applications of adhesives are taken into account, adhesive bonding must be considered as the most widely used method of holding various materials together.

The importance of the surface polarity and the surface characteristics for polymer adhesion has been considerably discussed in scientific literature [87]. A useful generalized theory of adhesion, however, can be built upon the basis of electrical attractions. The electrical attractions, resulting from uneven surfaces, which are not normally considered to be electrical, participate easily in attractive interactions if adhesives can be found that will wet them. Thus the reason that polyethylene and poly(tetrafluoroethylene) are difficult to bond is simply that available adhesives are thermodynamically more stable if their molecules attract one another than if they interact with low energy surfaces. The solution to this problem would

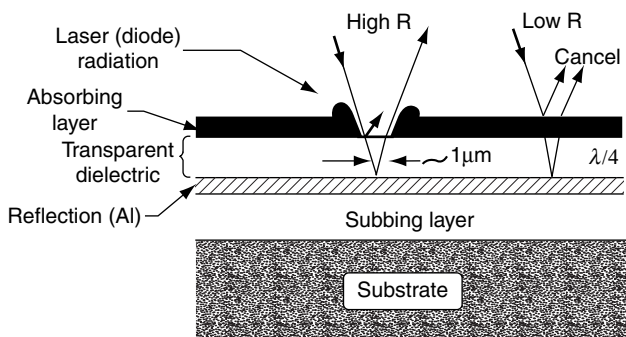


FIGURE 5.51 Trilayer structure of a typical ablative-mode optical disc.

therefore be to modify the surfaces of difficult-to-bond materials so that they become capable of strong electrical attractions. A number of processes are routinely used industrially for this purpose.

In general, for an adhesive to work it must start out in a fluid state to enable adequate wetting of the substrates to take place, and then the fluid state must be replaced by a solid state to enable the adhesive bond to gain strength. There are many types of adhesives varying in the way the liquid state is provided and/or the method of attaining the final solid state. In practice, there are, however, two ways of applying macromolecular adhesives. The adhesives may be applied as a nonpolymerized liquid (monomer, oligomer) that reacts after wetting the surface to form a polymer. This approach is typical of epoxies, phenolics, polyesters, and cyanoacrylates (see [Chapter 4](#)). The other technique is to apply the fully polymerized product, and this requires that the macromolecular compound be applied above the melting range, above its glass transition temperature, or in solution. Bond strength develops as the adhesive solidifies.

Adhesives currently on the market and used in significant quantities can be classified into four categories: solvent-based, water-based, 100% solids (hot melt), and radiation cured. Not all categories offer the same performance or processing benefits.

5.8.1 Solvent-Based Adhesives

Solvent-based adhesives are made by dissolving suitable solid materials in appropriate organic liquids. The solution is the liquid phase, which carries out the wetting of the substrates; then the solvent is removed by evaporation, leaving a solid adhesive film.

The progress of technology over the last 100 years has made available a number of organic liquids in large quantities, as well as a range of synthetic solids that can be dissolved in them. Various combinations of these materials form a substantial part of the adhesives industry, the choice of the solvent depending on what is to be dissolved, availability, cost, and health and environmental conditions.

In the U.S. converting industry, one- and two-component solvent-based adhesives are still the most widely used, accounting for nearly 80% of adhesive formulations. Many of these adhesives are typically polyester- or polyether-based urethanes (see [Chapter 4](#)) with isocyanate functionality that cure by reacting either with atmospheric moisture or a cross-linker. Polyether-based urethanes, while less expensive than polyester-based, do not provide the same strength and do not perform well in some processing environments or end uses.

The choice exists between using a one-part or a two-part formulation. One-part formulations are based on polyurethanes of very high molecular weight that are still soluble in petroleum-ester mixtures. Two-part adhesives are normally used where high cohesive strength and improved heat resistance are required and these comprise with the prepolymer terminated in some active group (such as polyether or polyester polyols) and as the second part either a multifunctional isocyanate (e.g., MDI) or an isocyanate

terminated polymer (e.g., PMDI) of rather lower molecular weight. These materials can be formulated to allow a variety of potlife times, with a typical maximum of two hours.

Polyurethane adhesives are most widely used for bonding elastomers, fabrics, and thermoplastics, and have found major uses in boot and shoe industry. Polyurethane adhesives continue to represent an excellent choice for bonding metal to plastics or rubbery adherents and are superior to many other adhesives at cryogenic temperatures, maintaining their shear strength and toughness at temperatures far below those that cause serious embrittlement of other adhesives. Polyurethane two-part adhesives also find high-performance engineering applications. High-performance uses, in fact, are a fast-growing segment because of the industry's desire to eliminate standard mechanical bonding methods such as nuts and bolts, screws, and welding.

The adhesive properties of polyurethanes may be attributed to the polar nature of the macromolecular compounds used in their formulation. Furthermore, the isocyanates present in the polyurethane compositions may react with any active hydrogen present in the adherent or with the films of water often present on the surfaces of materials such as ceramics, glass, and metals. These types of reactions result in enhanced anchoring of the adhesive and attainment of high bond strength.

There exists a large number of other solvent-based adhesives derived from synthetic polymers that are soluble in organic solvents. For example, substituted nylons (aliphatic polyamides)—typically, *N*-methoxymethyl nylons—are soluble in some alcohols and alcoholic mixtures and have been used to provide solution adhesives with good rust resistance. Such soluble nylons may be compounded with many thermosetting polymers to improve their properties to yield such outstanding characteristics as their resilience and peel strength.

Polyamides of enhanced solubility also result from the use of acids or amines containing large bulky side groups that prevent close packing of molecules (e.g., branched diamines and cyclohexane dicarboxylic acid) and copolymerization to give irregular structures (e.g., copolycondensation in acetic acid medium of caprolactam with ω -amino-undecanoic acid). Strong and versatile protective adhesives, and coatings are produced by mixing solutions of some polyamides with epoxy resins. The coatings are tough, hard, flexible and strongly adhering to a wide variety of surfaces such as wood, concrete, steel, glass, and many different kinds of plastics.

Many of the organic solvent-based adhesives are based on rubbery polymers, the main ones being natural rubber, polychloroprene, butadiene-acrylonitrile, styrene-butadiene, and polyisobutylene. In a typical method of manufacture, the rubber is placed in a heavy-duty mixer and solvent is added slowly till a smooth solution is formed. In some cases, the rubber is milled beforehand to reduce viscosity and produce smoother solutions. Depending on the rubber, the solvent can either be petroleum hydrocarbon of differing boiling ranges, aromatic hydrocarbon (usually toluene) or oxygenated solvents such as ketones or esters. Chlorinated solvents are used when nonflammability is required. Various resins are added to improve adhesion to different substrates. Antioxidants are added to improve ageing characteristics which fillers are often added to improve performance.

These organic solvent-based adhesives are very easy to apply and find wide application in general industry. Whenever a variety of different materials has to be stuck together quickly and easily, organic solvent-based adhesives will often be the answer. The footwear industry uses them for sticking soles to uppers and many other operations. The automotive industry uses them for stick-on trim and a variety of other jobs. Foam-seat manufacturers use these adhesives in brushable and sprayable form. Paper converters employ solvent-based permanently tacky adhesives in the manufacture of labels and sticky tapes.

A special type of organic solvent-based adhesive is the so-called contact adhesive. This makes use of the fact that certain elastomeric or rubbery solids (e.g., polychloroprene) have the property of autohesion, i.e., they can stick readily to themselves, especially if compounded with resins and containing small amounts of solvents. The bonding takes place by a diffusion process, the adhesive being applied to both surfaces to be bonded. Thus substrates may be coated with a contact adhesive, the adhesives can be allowed to dry till most of the solvent has evaporated (the dry adhesive film at this point will contain

residual solvent, often up to 7–10%, but the film will not adhere to another substrate) and the two adhesive surfaces can then be brought together, the bonding taking place immediately and without much pressure. Because of this property, contact adhesives find wide use in industry for easily sticking many different materials together without the need for clamping.

Although natural rubber was the first polymer used in contact adhesives, it has been almost entirely displaced in favor of synthetic polymers. The first to achieve prominence was polychloroprene, but this has later been joined and, for some purposes, displaced by polyurethane and acrylic copolymers.

It may be noted that contact adhesives are different from pressure-sensitive adhesives. The latter generally combine a high degree of inherent tackiness, for instantaneous bonding, with a high cohesive strength to facilitate removal of tape from a surface without leaving any residue. Typically, the adhesive is based on a film-forming elastomeric material such as SBR, polychloroprene, polybutadiene, and other normally tacky polymers, such as polyvinyl ethers and polyacrylates. Commonly, blends and combinations of various materials are needed to optimize initial tack, cohesive strength, and, of course, the actual adhesive properties of the substrate. Polyterpene resins and rosin esters are often used as tackifiers in many formulations. Pressure-sensitive adhesive tapes, for example, are composed of (1) the adhesive, (2) a primer coating that is applied to the plastic or metal foil surface, (3) a release coating on the backing to allow unrolling of the tape, and (4) a suitable backing material such as plastic, metal foil, paper, and nonwoven textiles.

5.8.2 Water-Based Adhesives

This class of adhesives contains some of the most traditional materials, for example animal glues and gums derived from natural sources, which are long-chain molecules, are soluble in water, and are either proteins or polysaccharides. Modern technology has brought other water-soluble materials into use; for example, poly(vinyl alcohol) adhesives, and a host of resins based on phenol, urea, and formaldehyde (see [Formaldehyde Resins](#) in [Chapter 4](#)).

Water-based adhesives also encompass emulsion and dispersion adhesives in which polymer chains are dispersed and stabilized into tiny particles or spheres in aqueous medium with the aid of surfactants. Within this category there are low-cost poly(vinyl acetate) and acrylics, and more expensive higher-performance urethanes, which are typically made of two components.

Because water-based adhesives contain little or no organic solvents, they offer manufacturers a strategy for compliance with volatile organic compound (VOC) regulations. The use of water-based systems is therefore growing quickly, particularly in applications that do not require high-performance properties.

Probably the most widely used industrial emulsion or dispersion adhesives are those based on poly(vinyl acetate), commonly referred to as PVA. These products are normally manufactured by emulsion polymerization whereby, basically, vinyl acetate monomer is emulsified in water with a suitable colloid-emulsifier system, such as poly(vinyl alcohol) and sodium lauryl sulfate, and, with the use of water-soluble initiator such as potassium persulfate, is polymerized. The polymerization takes place over a period of four hours at 70°C. Because the reaction is exothermic, provisions must be made for cooling when the batch size exceeds a few liters. The presence of surfactants (emulsifiers) and water-soluble protective colloids facilitates the process resulting in a stable dispersion of discrete polymer particles in the aqueous phase.

Plasticizers and thickeners are two of the materials most commonly used in the formulation of PVA-based adhesives, but many other modifiers may be needed, producing a very wide range of adhesives to meet specific requirements of a wide variety of applications.

PVA-based adhesives exhibit excellent adhesion properties and adhere to a host of different substrates such as metal, porcelain, wood, paper and various textiles. The adhesives are quick-setting, a property which shortens press and assembly times in manufacturing processes.

While a substantial proportion of emulsion adhesives are based on PVA, copolymer emulsion adhesives based on vinyl acetate ethylenes (VAEs) are becoming of increasing significance and

importance in the market place. These are produced by the copolymerization of vinyl acetate and 10–20% ethylene, the resulting polymer base possessing some superior properties over the PVA-based emulsions referred to above. These superior properties relate principally to the increased inherent flexibility of the dry VAE film, which enhances adhesion to many “difficult” surfaces. There also exist many alternate specialized emulsion adhesive systems for which a number of other polymers and copolymers are used as the formulating basis.

Generally, water-based adhesives are used where at least one of the substrate is porous, or permeable to moisture vapor. The two substrates to be joined are laminated while the adhesive is still wet, and the water escapes either by initial absorption into one of the substrates or by evaporation due to permeability.

Because of the need to remove water, most applications for aqueous adhesives are with materials that would allow transmission of water vapor. Hence the major uses are with paper, wood and fabric, either as binders or laminating adhesives. Typical applications of emulsion adhesives include the following: remoistenable gummed tape, tube winding, box manufacture, plywood manufacture, woodworking, bookbinding, abrasives manufacture, and as textile adhesives.

5.8.3 Hot Melt Adhesives

Hot melt adhesives are thermoplastics that when molten are applied to the substrates [89]. Setting is achieved rapidly, normally in a few seconds or less, leading to high production speeds, and for this reason melt adhesives are attractive for a number of applications. They are 100% solids, containing no solvents; this means no evaporation and no VOC emissions. Other advantages are indefinite shelf life, much reduced space requirements due to lower warehouse volume, and avoidance of drying areas.

Melt adhesives are based on thermoplastics, but usually contain a number of other components. The most commonly used melt adhesives are based on ethylene-vinyl acetate (EVA) copolymers, but polyethylene, polyesters, polyamides, and thermoplastic rubbers (e.g., styrene-butadiene block copolymers) are also used (see [Adhesive Bonding of Plastics](#) in [Chapter 2](#)).

Depending on the properties required, the vinyl content in the EVA copolymer may be varied and varying quantities of tackifying resins (e.g., rosin esters) and waxes are incorporated. Tackifying resins affect the adhesion at elevated temperatures, the time the adhesive takes to harden and the quality of final adhesion achieved. The main purpose of the waxes is to reduce the melt viscosity and thereby improve the wetting of the substrates.

The widespread use of hot melt adhesives includes bookbinding (soft cover binding of books and magazines), component assembly in electronics, consumer durables, automotive fields, and various applications in the packaging industry (e.g., carton sealing, bag making, labels), footwear manufacture (counters and toe puffs), woodworking, and the textile industry.

The main limitations of hot melt adhesives are their modest service temperature and modest load-bearing ability. Polyester and polyamide systems are usually much superior to EVA systems in both these respects.

5.8.4 Radiation-Curable Adhesives

The term radiation curable is applied to adhesives that cure when exposed to ultraviolet light (UV-curable) or electron beams (EB-curable). These forms of radiation have the correct energy to initiate polymerization of low-molecular-weight unsaturated resin. The type of cross-linking obtained with EB and UV radiation is very similar but the way the curing is brought about differs. The polymerization is not directly initiated by UV radiation and a photoinitiator is used to interact with the UV light and produce the initiating species. Electron beams, however, have higher energy, which is sufficient to initiate polymerization.

Electron beams are more penetrating than UV radiation and can thus be used to bond some opaque substrates that cannot be bonded with UV-curable adhesives. However, this advantage is offset by the

high capital costs of EB curing equipment, especially in comparison with UV lamps, which are both cheap and readily available.

Though potential UV-curable system [90] are many, only two have found significant commercial use in adhesives, namely, free-radical polymerization of acrylates and cationic polymerization of epoxies.

The essential ingredients of a free-radical adhesive formulation are an acrylate-terminated prepolymer and a photoinitiator. A wide range of prepolymers can be acrylated, including epoxies, urethanes, polyesters, polyethers, and rubbers. Those most commonly used in adhesive formulations are epoxy and urethane acrylates. Epoxy acrylates have properties similar to those of the parent epoxy resin, with excellent adhesion, chemical resistance, and toughness. Urethane acrylates, on the other hand, are noted for their high reactivity, good adhesion, flexibility, and tear resistance.

Acrylated prepolymers usually have high viscosities and require a diluent. This can be an acrylate monomer or a low-toxicity monomer that itself takes part in the curing reaction. The use of such reactive diluents results in changes to the viscosity, flexibility, and the speed of cure of the formulation.

Additives are commonly used to improve the performance of an adhesive. These might include adhesion promoters, fillers, light stabilizers, antioxidants and plasticizers. A drawback of acrylate-based formulations is the oxygen sensitivity, i.e., inhibition of curing by oxygen, which occurs due to quenching of the excited photoinitiator and scavenging of free radicals. The oxygen inhibition may be overcome by adding oxygen scavengers to the formulation. Other methods are nitrogen blanketing, the use of high intensity lamps, and varying the initiator type and concentration.

Cationic UV adhesive formulations typically contain an epoxy resin, a cure-accelerating resin, a diluent (which may or may not be reactive) and a photoinitiator. The initiation step results in the formation of a positively charged center through which an addition polymerization occurs (see [Epoxy Resin in Chapter 4](#)). There is no inherent termination and this may allow a high degree of post cure.

The advantages of a cationic adhesive formulation over that of a free radical one are the lack of oxygen sensitivity, less shrinkage on curing, and better adhesion. The disadvantages are that the photoinitiators are sensitive to moisture and basic materials and that the acidic species can promote corrosion. Consequently, the majority of UV formulations used in industry are acrylate based and cured by a free radical mechanism.

UV curing of adhesives offers several advantages over conventional methods of cure. These include significant productivity benefits arising from the low running costs of UV lamps and the very rapid cure of the adhesives. These adhesives also contain no solvents that are damaging to the environment. Requiring no heat, they are suitable for heat-sensitive substrates and are single component.

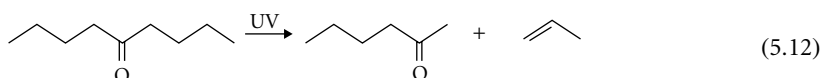
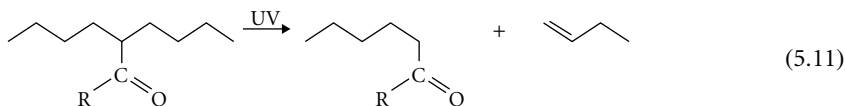
The disadvantages of UV adhesives are that one transparent substrate is normally required; they suffer from oxygen inhibition and only a limited depth of cure can be achieved. The latter problem has been tackled by the development of dual-cure adhesives. In these systems, two independent curing mechanisms are incorporated into a single system. Thus the adhesive is cured first to a chemically stable form by UV irradiation and subsequently led to full cure by a second means, for example, thermal cure.

UV curable adhesives are being used in a large number of industrial applications. Some of the most significant of them include plastics and glass bonding, as well as applications in electronics. These applications demand high-performance adhesives which bond to difficult substrates.

5.9 Degradable Polymers

Although there certainly has never been a great incentive for making unstable polymers, the idea of making degradable polymers has long existed due to its environmental significance, and quite a bit of effort has gone into research along these lines. There are two important ways of making a degradable polymeric material. One is to make the polymer sensitive to sunlight, which fractures its chemical bonds and breaks it down by photodegradation; the other is to make a polymer out of a material that is biodegradable.

To make plastics photodegradable, a material can be implanted that will absorb sunlight and becomes sufficiently reactive to attack the polymer molecules from which the material is composed. One other means of photodegradation is to incorporate in the polymer backbone suitable groups, e.g., carbonyl groups that absorb the ultraviolet (UV) component of the sunlight to form excited states energetic enough to undergo bond cleavage. Such processes (referred to as Norrish type II reactions) occur as follows:



The main problem in making a photodegradable polymer is that it is hardly possible to combine rapid degradation upon exposure to light in a landfill after use with a good light-stability of the polymer during service. This contradiction is probably the reason why this method never really caught on.

The difference between photodegradation and biodegradation lies in the possibility to create an environment (as in a landfill) completely different from that encountered under normal storage conditions; e.g., microorganisms that can destroy organic polymers may be added to a landfill. In spite of the fact that substantial research time was spent on studies in this field, it is claimed [91] that surprisingly little is understood about the molecular-level interaction between polymers and microorganisms. For polyesters, however, a number of interesting data are available. Esterases (ester-hydrolyzing enzymes) and some microorganisms are known to biodegrade polyester at a reaction rate depending upon the polyester structure. While many aliphatic polyesters, specifically poly(hydroxy fatty acids), are suited for biodegradation, the aromatic polyester (e.g., PET) do not possess this property.

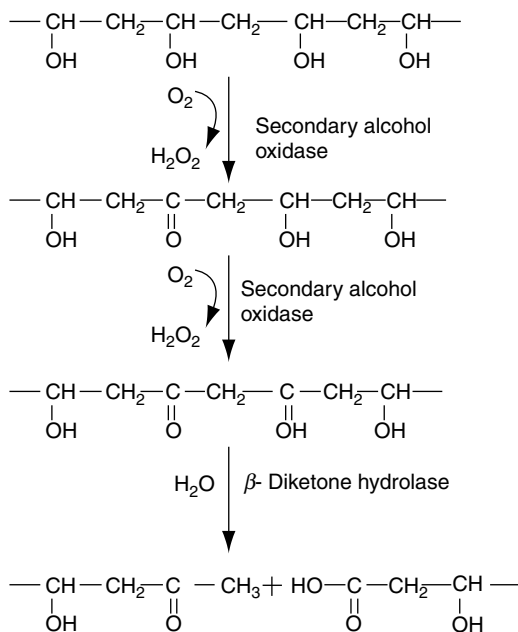
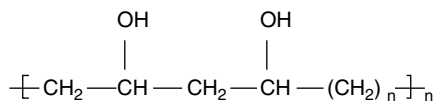


FIGURE 5.52 Mechanism of enzymatic depolymerization of poly(vinyl alcohol).

Poly(vinyl alcohol) is the most readily biodegraded, compared to other vinyl polymers, e.g., polystyrene, polyethylene, and polypropylene. Respirometric assays with mixed culture activated sludge have shown that poly(vinyl alcohol) is mineralized [92]. Extensive studies have been reported on the purification, characterization, and mechanism on degradation of poly(vinyl alcohol) by enzymes isolated from pseudomonas. The polymer is degraded as the sole carbon source by these organisms; the mechanism of action is summarized in Figure 5.52.

Poly(ethylene-co-vinyl alcohol) is a thermoplastic used extensively in laminates for food containers due to its excellent film forming and oxygen barrier properties. Limited evidence for the disappearance of the polymer was provided [93]. Whether or not the copolymer is biodegradable is apparently related to the size and distribution of the ethylene blocks.



Poly(vinyl acetate) and poly(ethylene-*co*-vinyl acetate) (EVA) are slowly biodegraded [94], particularly where there is a high percentage of vinyl acetate in the copolymer. Growth of fungi on EVA copolymers correlate directly with vinyl acetate content [95], which seems to suggest that a pathway wherein enzymatic hydrolysis of side-chain ester groups occurs instead of the oxidative chain cleavage required for polyolefins may play a role.

5.9.1 Packaging Applications

The polymer poly(hydroxybutyrate) (PHB) is a natural polymer made by a wide range of microbes, such as the bacterium *Alicigenes eutrophus*, as a convenient way of storing energy (in the same way that human beings store energy as fat). PHB is a crystalline, thermoplastic polyester of 3-hydroxybutyric acid [$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COOH}$]. It has been commercialized by ICI under the trade name Biopol. Often it is copolymerized with hydroxyvaleric acid $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{COOH}$, to produce poly(3--hydroxybutyrate-*co*—3-hydroxyvalerate). The copolymerization increases the percentage of amorphous regions that are readily attacked by hydrolytic degradation, thereby increasing degradation rates.

The properties of the copolymer can be tailored to make it suitable either for molded articles such as shampoo bottles, or thin films for plastic envelopes or carrier bags. However, the polymer is costly, a container made of Biopol being about seven times more expensive than polyethylene. This polymer is now in production and used for packaging, agricultural products, and disposable items of personal hygiene.

Another approach to making biodegradable plastics for packaging consists of mixing small amounts of biodegradable polymers (e.g., starch) with a regular polymer (e.g., polyolefin), in order to make the end product destroyable as well. Starch is of interest as a biodegradable material because of its low cost, its availability as agricultural surplus raw material, and the thermoprocessability of the blend using conventional plastics-processing equipment.

In the early 1970s, work was in progress at two noncommercial centers to create a biodegradable plastic material that would be acceptable to the packaging industry. One such center was the USDA laboratories in Peoria, Illinois, as part of a program of work aimed at finding nonfood markets for farm products. The Peoria project approached its target by adopting starch as the matrix natural polymer, gelatinizing the starch by the action of heat and water, and then seeking synthetic polymeric additives that would make the mix processable on familiar plastics machinery. The products thus had starch gel as the continuous phase.

The other center, at Brunel University in the United Kingdom, developed the complimentary technique of using polyolefin polymers as the continuous phase with particulate starch additives as a filler. The starch component was usually below 10%. Microbes digest the starch in such product, leaving a flimsy plastic lace that disintegrates mechanically. The starch being in small amounts hardly alters the properties of the original polymer and the product can be processed on existing machinery without costly alterations.

One blend of polyethylene and starch incorporates an auto-oxidant that reacts with metal salts in soils or other environments to form peroxide radicals. The radicals degrade the polyethylene polymer chains into smaller oligomers susceptible to mineralization [96]. The starch is treated with a silane coupling agent for compatibility with polyethylene, and an unsaturated ester such as soya or corn oil is used as the auto-oxidant. Later technology has considered temperature triggers based on a composting regime [96].

The USDA technology mentioned above produces blends of gelatinized starch with nonbiodegradable components, such as ethylene and acrylic acid [97]. Blown films containing up to 60% starch are made and ammonia is added in the process. Many companies are commercializing thermally processed starch blends containing high percentages of starch for a wide variety of applications (e.g., Novon, Novamont).

Mixtures of starch with other polymers, including PET, have been studied [98], but no commercialization of the latter mixture is known.

Polyethylene can be made photodegradable by copolymerizing ethylene with a small percentage of carbon monoxide so that carbonyl groups are built into the long chain $\text{—(CH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{)—}$. Polymers containing 1% of carbonyl groups lose their strength after two days in the sun. The polymer is thus decomposed into short chains [Equation 5.12] that microbial enzymes can digest.

Another approach to making photodegradable plastics is to use photosensitizers such as iron and nickel dithiocarbamates. These compounds can absorb photons to produce free radicals that trigger chain reactions leading to polymer degradation. The stability of a polymer film can be regulated by the amount of photosensitizer used. Polyethylene film used for mulching the soil in vegetable growing can thus be timed to decompose and disappear at the end of the time of harvesting.

5.9.2 Medical and Related Applications

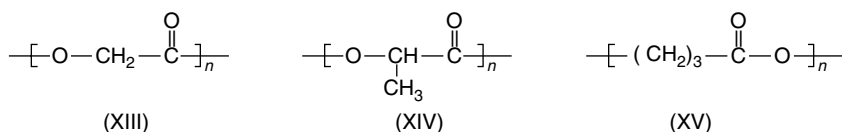
Biodegradability is often an important consideration in the development of biomedical, pharmaceutical, and agricultural products for a number of applications. Biodegradable polymers have been formulated for uses such as controlled release and drug-delivery devices, surgical sutures, scaffolds for tissue regeneration, vascular grafts and stents, artificial skin, and orthopedic implants.

5.9.2.1 Synthetic Polymers

Degradable, synthetic polymers that are commonly known in the medical field include poly(α -hydroxy esters), poly(ϵ -caprolactone), poly(ortho esters), polyanhydrides, poly(3-hydroxy butyrate), polyphosphazenes, polydioxanones, polyoxalates, and poly(amino acids).

Poly(glycolic acid) (PGA) and poly(lactic acid) (PLA) are examples of poly(α -hydroxy esters.) PGA is a highly crystalline, hydrophilic, linear aliphatic polyester (XIII). As such, it has a high melting point and a relatively low solubility in most common organic solvents. PGA degrades primarily by bulk erosion. This occurs through random hydrolysis of its ester bonds.

The degradation of PGA is bimodal with the first phase of degradation occurring by diffusion of water to the amorphous regions followed by hydrolysis. The second phase begins as water penetrates and hydrolyzes the more crystalline regions. For PGA surgical sutures, mass loss occurs primarily during the second phase, completing the entire process between 4 and 12 weeks. The rate of hydrolysis in vitro can be controlled by varying the pH. A more basic or acidic environment drives hydrolytic cleavage.



The linear aliphatic polyester, PLA (XIV) is chemically synthesized by condensation polymerization of the free acid or catalytic ring-opening polymerization of the lactide (dilactone of lactic acid). The ester linkages in the polymer are sensitive to both enzymatic and chemical hydrolysis. PLA is hydrolyzed by many enzymes including pronase, proteinase K, bromelain, ficin, esterase, and trypsin. The degradation rate of PLA also varies with varying pH. The amount of lactic acid released during the course of PLA degradation is very small but increases rapidly as PLA is broken down to low molecular weight oligomers.

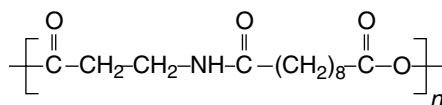
PLA is primarily considered for medical implants and drug delivery, but broader applications in packaging and consumer goods are also targeted. An attractive feature of this material is the relatively low cost of the monomer, lactic acid, which can be derived from biomass (fermentation), coal, petroleum, or natural gas.

Copolymerization of poly(α -hydroxyesters) provides a means to control physical and mechanical properties of the product. The degradation rates are highly dependent on the relative amount of each monomer. Copolymers with high or low ratios of comonomers are much more stable to hydrolytic attack than copolymers with a more equimolar ratio, due to their greater crystallinity.

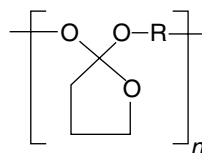
Multiple uses of poly(lactic acid), poly(glycolic acid) homopolymers, and poly(lactic-co-glycolic acid) copolymers have been described including sutures, vascular grafts, drug carriers, and scaffolds for tissue engineering (discussed below). This is due in part to the FDA approval of these polymers for use as implantable materials.

Poly(ϵ -caprolactone) (PCL) is a semicrystalline aliphatic polyester (XV), synthesized by ring-opening polymerization of ϵ -caprolactone. PCL has been shown to degrade by random hydrolytic scission of its ester groups, and under certain circumstances by enzymatic degradation. Chemical hydrolytic rates of PCL homopolymers are very slow, particularly when compared with polyglycolic acid and poly(glycolic-co-lactic acid). PCL has a low glass transition temperature of -62°C , existing always in a rubbery state at room temperature, and a melting temperature of 57°C . It has been postulated that these properties lead to a high permeability of PCL for controlled release agents.

A number of amino acid derivatives have been synthesized primarily for biomaterial applications as implants and for controlled release. These polymers include amino acid-based polyanhydrides and polyesters. Poly(amide-anhydride) of structure (XVI), for example, is formed from β -alanine and sebacoyl chloride (that is, amino acid and diacid chloride) under anhydrous conditions in the presence of an acid acceptor. The premise upon which this class of polymers is designed is that the anhydride linkage will hydrolyze rapidly at the surface of a material and more slowly toward the center, providing for controlled release. The primary mechanism for depolymerization is surface erosion via chemical hydrolysis rather than enzymatic depolymerization. The polyanhydrides of aromatic diacids have advantages when compared with aliphatic polymers, including longer release and degradation times and higher mechanical strength and stability.



(XVI)



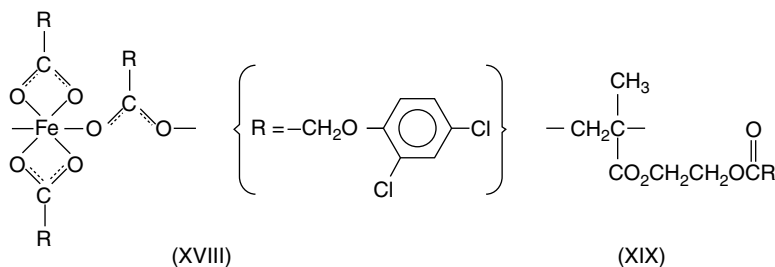
(XVII)

Poly(ortho esters) (XVII) contain acid-labile linkages in the polymer backbone. As with the polyanhydrides discussed above, poly(ortho esters) are a class of polymers that can degrade heterogeneously by surface erosion. These polymers lose material from the surface only, while retaining their original geometry. As such, their primary use is in drug delivery.

5.9.2.2 Controlled Release Agents

Controlled release refers to the use of polymers containing agents of agricultural, medicinal, or pharmaceutical activity, which are released into the environment of interest at relatively constant rates over prolonged periods [99,100]. In the agricultural field, degradable mulches to promote crop growth are composed of combinations of natural polymers (which degrade readily in the presence of soil microorganisms) and synthetic polymers. Examples are starch-graft-poly(methyl acrylate) and block copolymers of amylose or cellulose with polyesters. At the end of the growing season, such mulches may be plowed directly into the soil along with crop residues.

Another application involves binding of agricultural chemicals in polymer formulations for slow release at a rate effective for their intended purpose avoiding the risk of the reagents being washed away by rain or irrigation. For example, the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) has been incorporated into polymers either as a chelate with iron (XVIII) or as a hydrolysable pendant ester group on a vinyl polymer (XIX).



A different strategy for controlled release is based on polymer permeability other than degradation. The active reagent may be encapsulated within a polymeric membrane or in a strip, as shown in Figure 5.53. Ideally the reagent is contained in the reservoir as a saturated solution with excess in suspension. This allows diffusion through the membrane at constant rate without loss of activity. Alternatively, the reagent may be dispersed in a polymer matrix and released to the environment by diffusion or extraction. A variety of membrane and matrix devices are commercially available [99]. Pheromone release strips for insect control and household fly and cockroach strips for release of insecticide are also in commercial use.

Encapsulated pharmaceuticals have been available for many years. Reservoir strips called transdermal patches are used to release drugs through the skin; for example, nitroglycerin to treat angina or scopolamine to combat motion sickness. Implanted polymeric matrix devices, including some made with degradable polymers to release the drug through surface erosion, are available. Degradable polyesters, described above, are used as disappearing surgical sutures. The inorganic polyphosphazene, $[-N=PCl_2-]_n$, with amino acids, esters, and steroids in place of the chlorine atoms, are of interest for slow release of the steroid, the other degradation products (amino acid, ester, phosphate, and ammonia) being nontoxic.

5.9.2.3 Tissue Engineering

An interesting application of biocompatible and biodegradable polymers is in the field of tissue engineering, which involves the creation of natural tissue with the ability to restore missing organ function.

The problem of donor scarcity precludes the widespread utilization of whole organ transplantation as a therapy to treat many diseases. Not only is finding a suitable donor difficult, but once found it is a costly coordinated effort to harvest and transport the required organ. Scientists and physicians have therefore sought a feasible alternative to organ transplantation. Materials such as metals, ceramics, and polymers have been used extensively to replace the mechanical function of hard tissues such as cartilage and bone. Devices constructed primarily of polymers, such as artificial hearts and membrane oxygenators, have also been used to partially replace organ function, at least on a temporary basis.

Tissue engineering is a potential alternative to existing therapies, as it would allow the restoration of organ function by creating complete natural tissue, with the required mechanical or metabolic features in vivo [59]. Though still in its experimental stages, the use of tissue engineering techniques to regenerate organs has the potential to affect the quality and length of many lives. The technique can be applied for

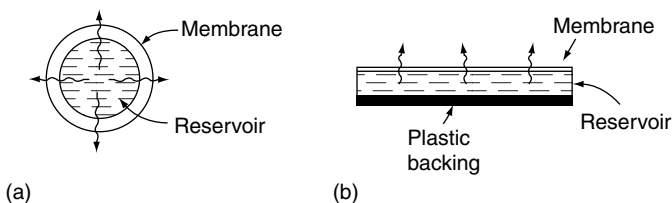


FIGURE 5.53 Membrane-controlled release devices: (a) microencapsulation and (b) strip.

virtually any tissue and organ in the human body, e.g., in bone repair, cartilage regeneration, wound healing, ocular diseases, mandible reconstruction, and androgenesis.

The creation of natural tissue may be achieved either by transplanting cells seeded into a porous material (Figure 5.54a and b) or, in some cases, by relying on in-growth of tissue and cells into such a material (Figure 5.54c). The process by which regeneration is effected by in-growth from surrounding tissue is known as tissue induction. The process can be facilitated or enhanced by the release of chemotactic agents from the porous material which attract cells to the area of regeneration (Figure 5.54d). Transplanted cells may be autogeneic (from the same genotype), allogeneic (from the same species but with a different genotype), or xenogeneic (from a different species). Autogeneic cells transplantation is the most preferable choice since it avoids many of the problems associated with immune rejection of foreign tissue.

There has been a great deal of research involving cell culture on biodegradable materials and development of techniques to manufacture degradable polymer scaffolds. Tissue engineering using transplantation of autologous (i.e., from the same patient) cells has been studied to restore the function of tissues such as cartilage, bone, skin, nerve, kidney, and liver, as this method of restoring organ function offers a number of advantages over whole organ transplantation, the two most important of these being overcoming the problem of donor scarcity and the reduced risk of rejection. Extensive research has also been performed with encapsulated xenogeneic pancreatic islets to treat insulin deficiencies in diabetics. In this case, the polymer acts both as a cell substrate and as a permanent protective barrier to the immune system.

Stem cell therapy is one very interesting strategy for tissue regeneration because it combines the potential of stem cells to develop into a particular functional tissue with the possibility of donor cell coming from the same patient, thus eliminating adverse immune response. Adult human stem cells are of particular interest, e.g., mesenchymal stem cells, which can develop into bone cartilage tissue and others [102]. Autologous stem cell treatment is carried out by the extraction of a small number of stem cells followed by their in vitro cultivation to obtain a sufficient large number, which can then be re-implanted with a scaffold and stimuli. The actual development is strongly dependent on a variety of biological regulation systems, e.g., the presence of growth factors, nutrients, cell-cell interaction, cell-matrix interaction, pH, and electrolytes [103].

The scaffold material should possess a number of properties like biocompatibility, biodegradability, mechanical strength, porosity, potential of entrapment and release of pharmaceutically active agents, and an easy processability for the clinician. Since safety is a critical issue and similar to new pharmaceuticals, regulatory agencies (e.g., FDA) need to approve the use of the scaffold. Materials already approved for scaffolds include poly(DL-lactide) (PLA), poly(DL-lactic acid-co-glycolic acid) (PLGA) and its block copolymers with poly(ethylene glycol) (PEG) [104]. However, the in vitro systems do not require biodegradability, but well defined material properties are desired during the whole cell cultivation process. Hydrogels can provide all these properties when choosing the right chemistry. They can provide softness, permeability for water, nutrients, metabolites or pharmaceutical active agents, and they show certain mechanical strength, which enables them to simulate living tissue. Therefore, they are excellent scaffolds for tissue engineering as well as drug delivery devices [105].

Recent research in polymeric biomaterials for engineering skeletal tissues and/or soft tissues such as muscles or lungs is focused on development of three-dimensional (3D) biodegradable polymer scaffolds [106]. A candidate for construction of such 3D polymer scaffolds is a fiber mesh consisting of individual polymer fibers woven or knitted into 3D patterns of variable pore size [107].

In order to enhance the bioactivity and potential osteoconductivity of bioresorbable polymer scaffolds, bioactive glass becomes a candidate material to be used as a coating, effectively forming a polymer/glass composite structure. Another reason to combine a bioactive glass with biodegradable polyesters is to control undesirable hydrolytic degradation characteristics of the polyesters such as rapid internal degradation and degradation-induced morphological and compositional changes. These considerations have led to the development of a new hybrid composite material concept based on using biodegradable polymer scaffolds coated with tailored bioactive glass layers [108]. A commercial bioactive glass is named

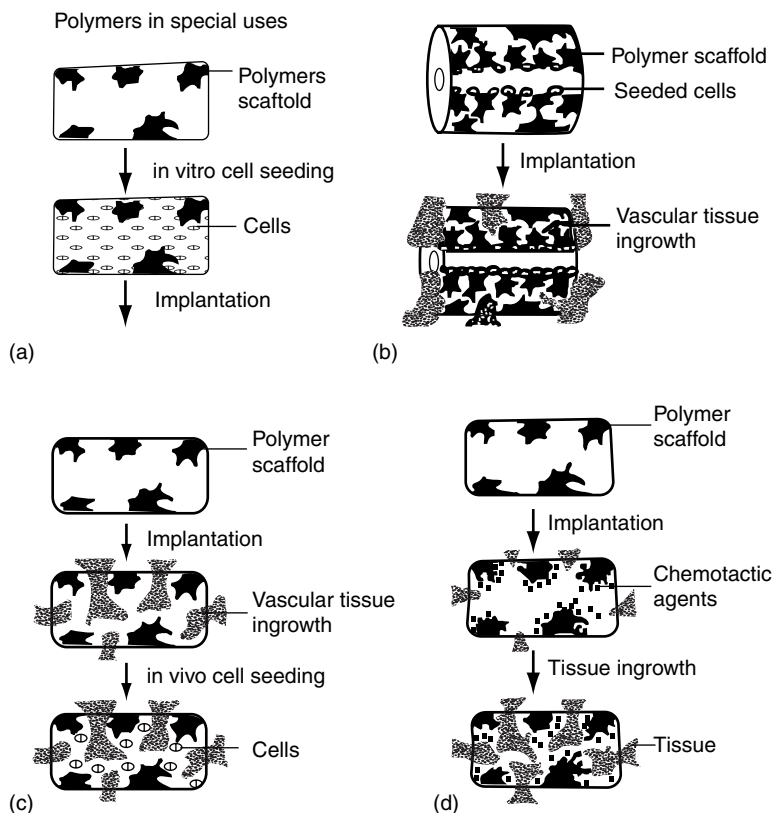


FIGURE 5.54 Schematic diagram of various regeneration techniques: (a) cell transplantation into porous scaffolds to regenerate tissues such as cartilage; (b) cell seeding into scaffolds with an annular space and subsequent tissue in-growth to regenerate tubular tissues; (c) prevascularization of scaffolds and subsequent cell seeding to regenerate metabolic organs such as liver; (d) tissue induction via release of chemotactic agents that attract the desired cells into a porous scaffold. (After Thomson, A. C., Wake, M. C., Yaszemski, M. J., and Mikos, A. G. 1995. *Adv. Polym. Sci.*, 122, 265. With permission.)

Bioglass®, which has the following composition by weight: 45% SiO₂, 24.5% Na₂O, 24.5% CaO, and 6% P₂O₅. When in contact with body fluids, this bioactive glass rapidly (2 h) forms a thin surface layer of calcium phosphate that stimulates cellular infiltration and osteointegration of the bioactive glass to the surrounding tissue by processes of osteoconduction, thus promoting bone regeneration [109].

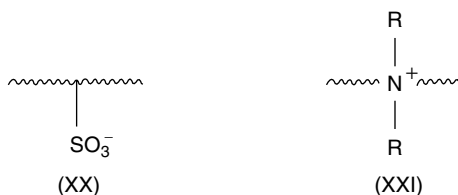
5.10 Ionic Polymers

Ionic polymers are polymers containing chemically bound ions within their structure [110–116]. These are specialist materials, some of which have limited, though important, commercial applications. Those containing few ions are melt-processable thermoplastics called ionomers; those containing many ions are either water-soluble polymers called polyelectrolytes or crosslinked polymers containing ionic groups called ion-exchange resins. Polyelectrolytes and ion-exchange resins are, in general, intractable materials and not processable on conventional plastics machinery.

Ionic polymers may be classified according to the type of the bound ion, its position within the structure, and the amount of bound ions present along a given length of polymer chain. They may be further classified according to the nature of the counterion or the nature of the supporting polymeric backbone.

The bound ion is usually either an anion such as sulfonate ($-\text{SO}_3^-$), phosphonate ($-\text{PO}_3^{2-}$) or carboxylate ($-\text{CO}_2^-$) or a cation such as quaternary ($-\text{NR}_3^+$) or amine ($-\text{NH}_3^+$). But both types can occur together and the polymer is then said to be ampholytic. In each case, the polyion may be strong or weak according to the degree to which it ionizes. For example, polysulfonates and quaternary type polyions are strong, polycarboxylates and amine type polyions are weak, while polyphosphonates are intermediate in nature.

The bound ion can be pendant to the polymer's covalent backbone, as in a polysulfonate (XX) or it can be integral or enchained, as in an ionene (XXI)



Almost any conventional polymer can be modified to form an ionic polymer of the pendant type. However, ionic polymers of the integral type, like the ionenes, are specialized structures whose backbones can exist only in the ionic form.

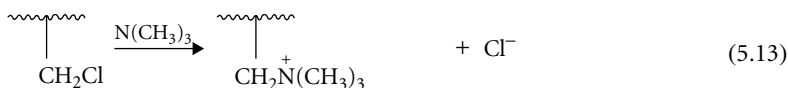
Ionic polymers contain counterions that neutralize the charges on the bound ions. The counterions may be grouped into three types: (1) univalent, (2) di- or trivalent and (c) polymeric. Polymers with polymeric counterions are often called polysalts, polyelectrolyte complexes, polyion complexes, simplexes, or coacervates.

The methods used for synthesis of ionic polymers can be divided mainly into three types: (1) direct synthesis, (2) post-functionalization of a standard preformed polymer, and (3) post-functionalization of a special preformed polymer.

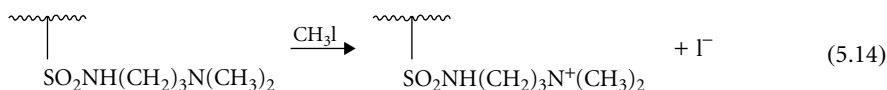
Direct synthesis is used for polyelectrolytes such as carboxy polymers, e.g., poly(acrylic acid) and poly(methacrylic acid), which are probably the most common ionic polymers of all. Post-functionalization of pre-formed polymers is a frequently used synthetic method, provided that the polymer is sufficiently reactive. Common examples are the sulfonation of polystyrene and the grafting of thioglycolic acid on to polybutadiene using free radicals.

Special post-functionalizable copolymers have also been used to derive acid ionomers by hydrolysis, thus avoiding the difficulties of copolymerizing ionic and nonionic monomers. To this end there are many examples where carboxylic acid polymers are formed by hydrolyzing copolymers containing acrylate esters, acrylonitrile, or maleic anhydride. As described later, a sulfonic acid ionomer, Nafion, is formed by hydrolysis of tetrafluoroethylene copolymerized with a sulfonyl fluoride.

All of the aforementioned ionomers are anionic polymers. Cationic polymers are less common, though equally important. Pendant cations are usually of the quaternary ammonium type and made by a multi-step post-functionalization in which a precursor containing labile chloride is reacted with a tertiary amine:



Sometimes, the inverse of this is also done when a pre-formed polyamine is quaternized by reacting with an alkyl halide:



5.10.1 Physical Properties and Applications

Synthetic ionic polymers have three distinctive properties that dictate their usage: (a) ionic cross-linking, (b) ion-exchange capability, and (c) hydrophilicity. Major applications for organic ionic polymers in relation to their ion content and dominant property are summarized in Table 5.14.

5.10.1.1 Ionic Cross-Linking

Since the ions in ionic polymers are held by chemical bonds within a low dielectric medium consisting of a covalent polymer backbone material with which they are incompatible, the polymer backbone is forced into conformations that allow the ions to associate with each other. Because these ionic associations involve ions from different chains they behave as crosslinks, but because they are thermally labile they reversibly break down on heating. Ionomers therefore behave as cross-linked, yet melt-processable, thermoplastic materials, or if the backbone is elastomeric, as thermoplastic rubbers. It should be noted that it is with the slightly ionic polymers, the ionomers, where the effect of ion aggregation is exploited to produce meltprocessable, specialist thermoplastic materials. With highly ionic polymers, the polyelectrolytes, the ionic cross-linking is so extreme that the polymers decompose on melting or are too viscous for use as thermoplastics.

Two types of ionic aggregates are found in ionomers, called multiplets and clusters, which coexist in equilibrium within the matrix of covalent backbone material. The multiplets, very small and very numerous, are associations of ion-pairs up to eight in number that are purely ionic and are devoid of trapped segments of the covalent backbone, while the clusters are large associations of these multiplets between which are trapped segments of the backbone. Evidence for this theory of microphase separation into multiplets and clusters is provided by many types of physical measurement, the important techniques being small-angle x-ray scattering, and infrared and Raman spectroscopy.

5.10.1.2 Ion-Exchange

Ionic polymers contain two types of ions, namely bound ions, which are part of the structure, and the counterions, which are free. In a medium in which the ionic polymer is insoluble, the counterions are exchanged for similar ions from the surrounding medium and an equilibrium is established, the kinetics of the process being dependent on factors such as the physical form of the insoluble polyion, its porosity, and surface area. The fundamental fact in this exchange is that the counterions have free movement into

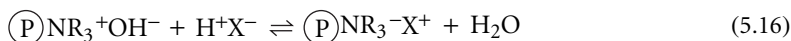
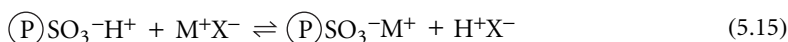
TABLE 5.14 Applications of Organic Ionic Polymers in Relation to the Amount of Ion Present

Ion Content (equiv/kg)	Designation	Dominant Property	Application	Example
> 0.5	Ionomer	Ionic cross-linking	Thermoplastic	Ethylene-acrylic acid copolymer
1–1.5	Ionomer	Ion-exchange	Membranes (electrodialysis, etc.)	PTFE copolymer (Nafion, Flemion)
1–1.5	Ionomer	Hydrophilicity	Membranes (reverse osmosis	Sulfonated polyether- sulfones
> 4	Polyelectrolyte	Water solubility	Thickeners, dispersants, flocclulants and sizes	Polyacrylic acid or copolymer
> 4	Polyelectrolyte (cross-linked)	Ion-exchange	Ion-exchange resins	Sulfonated polystyrene aminated polystyrene
14	Polyelectrolyte	Ionic cross-linking	Dental cements	Polyacrylic acid

and out of the polymer, while ions of the same type of charge as the bound ion do not. This barrier to ion movement is known as Donnan exclusion.

The property of ion-exchange has important consequences and three different types of application depend on it. They are (1) ion-exchange resins, (2) ion-exchange membranes, and (3) heterogeneous catalysis.

Ion-exchange resins are insoluble beads of an ionic polymer. Their bestknown use is in deionization or demineralization of tap water to distilled water. In this process, the water is contacted with two types of resin, one a polyacid and the other a polybase, so that the net effect is to exchange M^+ and X^- from the tap water for H^+ and OH^- , i.e., H_2O , from the polyion beads:



To be effective, ion-exchange resins should have high ionic content. They are therefore polyelectrolytes and, since polyelectrolytes are inherently water-soluble, they are chemically cross-linked during manufacture to make them insoluble. When immersed in water they undergo swelling, which facilitates rapid ion-exchange. The degree of swelling is, however, inversely related to the density of the cross-links.

A polyion in the form of a thin membrane is used as ion-exchange membrane in another application of the ion-exchange phenomenon. When exposed to an electrolyte, an ion-exchange membrane will allow counterions to pass through it, but will act as a barrier to the complementary ion, and is therefore said to be permselective. Thus a polyanionic membrane will allow passage of cations and a polycationic membrane that of anions, so that under the influence of an electric current, continuous fluxes of cations and anions, respectively, can be set up across these membranes. This principle is exploited in electrodialysis and in chlor-alkali cells as described later.

The dialyzer used for desalination of water by electrodialysis (Figure 5.55) is an electric cell divided into a series of sub-cells that are separated by alternate polyanion and polycation membranes. While the ions move under the influence of the applied electric potential, the complimentary permselectivities of the ion-exchange membranes insure that salt is removed from alternate sub-cells and concentrated in the others. Desalination dialyzers used in practice have up to 100 such sub-cells.

Other applications of dialyzers include concentration of brine and the desalting of cheese whey. (It is important not to confuse electrodialysis with ordinary dialysis, which is not an ion-exchange process but

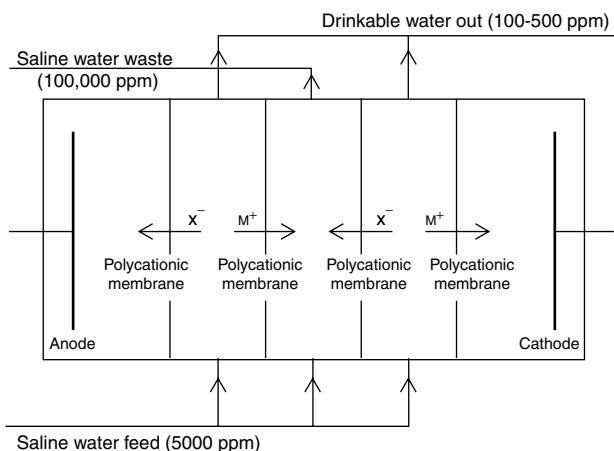


FIGURE 5.55 Desalination of water by electrodialysis.

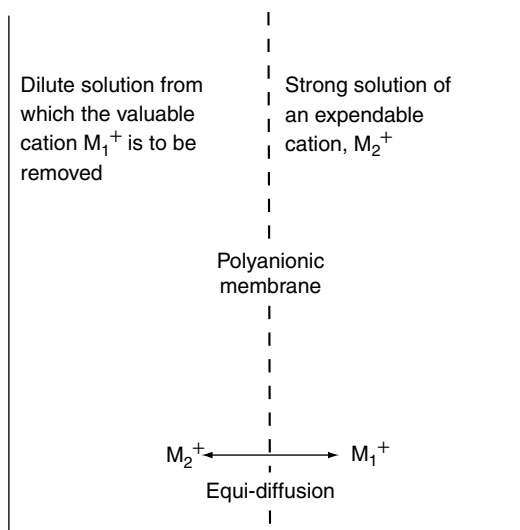


FIGURE 5.56 Ion-exchange dialysis.

is a separation based on differences in size and hence diffusivity between large and small molecules through a membrane, which, generally speaking, is not ionic.)

A related application of ion-exchange membrane is in ion-selective electrode. Thus when an electrode with an ion-exchange membrane encasing is immersed in an ionic medium, it will develop a potential proportional to the activity of the ion to which the membrane is permselective.

A high ion content is not necessary for an ion-exchange membrane, since its function is not governed by its exchange capacity. Though a high ion content can be advantageous as it decreases the electrical resistance, it can in fact be counterproductive if the membrane is so highly swollen by water that its permselectivity is reduced. The ion content of an ionexchange membrane is thus often intermediate between that of an ionomer and an ion-exchange resin.

While chemical cross-linking is used for ion-exchange resins to limit this swelling or to prevent the resin from dissolving, this method is generally not desirable for membranes, because cross-linking interferes with the process of membrane fabrication.

Ion-exchange dialysis (or Donnan dialysis) like ordinary dialysis is a diffusion-controlled separation process, but unlike the latter it involves ionexchange and so needs an ionic membrane (though without an applied current). If a polyanionic membrane is used, as shown in Figure 5.56, the cations diffuse each way across the membrane but the anions cannot so that, in effect, cations are separated as they swap over, but the amount of electrolyte on each side of the membrane remains constant. This type of dialysis, using continuous cells, is being developed as a means of stripping and concentrating radioactive ions from dilute solutions of radioactive wastes.

5.10.1.3 Hydrophilicity

Ionic polymers are hydrophilic. Those of moderate ion content swell on contact with water and those of high ion content dissolve, unless they are cross-linked. With moderately ionic polymers, which swell without dissolving, the hydrophilicity has the advantage of making the structure more permeable to ions for ion-exchange. The hydrophilicity of moderately ionic polymers leads to another type of membrane application, that of reverse osmosis.

The method of reverse osmosis involves application of pressure to the surface of a saline solution, thus forcing pure water to pass from the solution through a semipermeable membrane that does not permit passage of ions. Since the natural osmotic pressure tends to force the water from the region of low ionic concentration to that of the high, to achieve a flow in the opposite direction, as in reverse osmosis, a pressure has to be applied exceeding the osmotic pressure.

In the process used for desalination, a saline, brackish water or sea water is forced at very high pressure through a hydrophilic membrane resulting in water of drinkable quality (Figure 5.57). Reverse osmosis is also utilized for recovering waste water for paper mill operations, pollution control, industrial water treatment, chemical separations, and food processing.

The compartments indicated in Figure 5.57a are a schematic representation of reverse osmosis process. In practice, the reverse osmosis process is conducted in a tubular configuration system (Figure 5.57b). Raw waste water flows under high pressure (greater than osmotic pressure) through an inner tube made

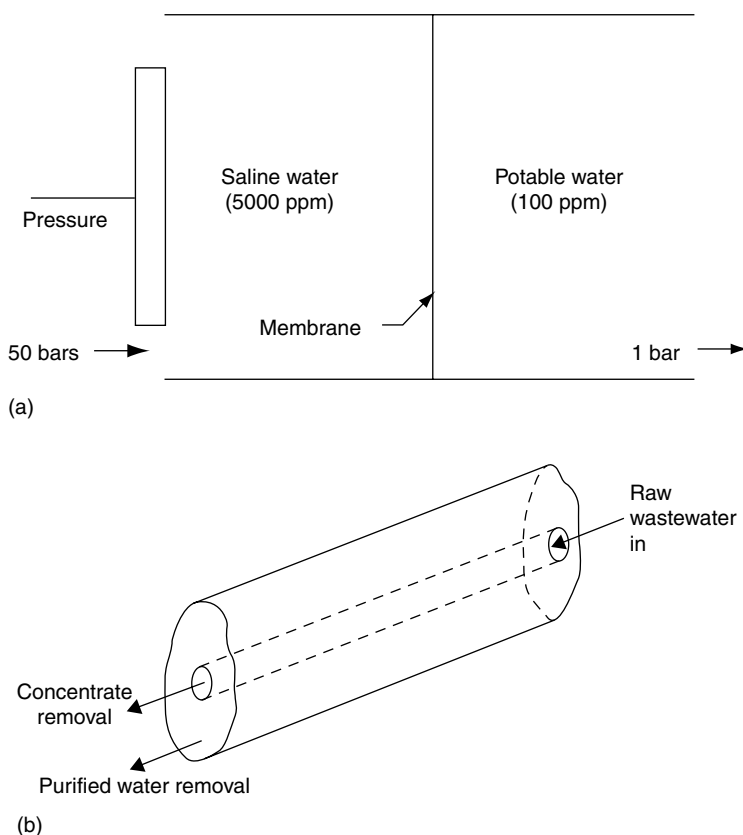


FIGURE 5.57 (a) Schematic representation of reverse osmosis process. (b) Tubular configuration system for wastewater treatment by reverse osmosis.

of a semipermeable membrane material and designed for high pressure operation. Purified water is removed from the outer tube that is at atmospheric pressure and is made of ordinary material.

Although the membrane used for reverse osmosis may be ionic and ion-exchange can occur, there is, however, no overall transmission of salt because of Donnan exclusion (and unlike electrodialysis no electric current is applied). Thus, while an essential requirement of a membrane for reverse osmosis is hydrophilicity, it need not be ionic. In fact, the most successful reverse osmosis membranes developed are made of nonionic cellulose acetate. Certain ionic polymers, such as the sulfonated polyaromatics, have been used because of their greater chemical stability and resistance to biological degradation.

Several mechanisms have been proposed to explain reverse osmosis. According to the preferential sorption-capillary flow mechanism of Sourirajan [114], reverse osmosis separation is the combined result of an interfacial phenomenon and fluid transport under pressure through capillary pores. Figure 5.58a is a conceptual model of this mechanism for recovery of fresh water from aqueous salt solutions. The surface of the membrane in contact with the solution has a preferential sorption for water and/or preferential repulsion for the solute, while a continuous removal of the preferentially sorbed interfacial water, which is of a monomolecular nature, is effected by flow under pressure through the membrane capillaries. According to this model, the critical pore diameter for a maximum separation and permeability is equal to twice the thickness of the preferentially sorbed interfacial layer (Figure 5.58b).

From an industrial standpoint, the two basic parameters characterizing reverse osmosis systems for a given separation are: (1) rejection factor, which involves the choice of the appropriate chemical nature of the film surface, and (2) water flux, which depends on methods for preparing films containing the largest

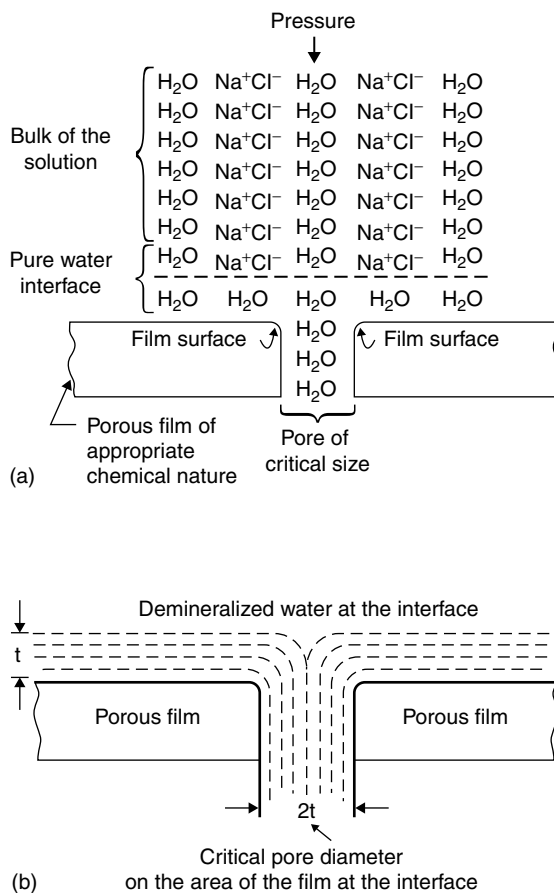


FIGURE 5.58 (a) Schematic representation of preferential sorption capillary flow mechanism. (b) Critical pore diameter for maximum separation and permeability. (After Agarwal, J. P., and Sourirajan, S. 1969. *Ind. Eng. Chem.*, 61, 62. With permission.)

numbers of pores of the required size. This approach is the basis of the successful development of the Sourirajan-Loeb type of porous cellulose acetate membranes for desalination and other applications.

To achieve high flux in reverse osmosis, the membrane should have a high surface area and be very thin ($0.02\text{--}1.0\text{ }\mu\text{m}$), but to withstand the high applied pressure it also needs to be very strong. To meet these requirements, which are in conflict, the semipermeable membrane is used as a skin mounted on a support, which is another membrane that is very porous, like a filter paper, and that is nonselective, and very thick ($> 100\text{ }\mu\text{m}$). In some such bilayers each layer is of the same polymer and the membrane is then called integral or asymmetric, but in others the layers are of different polymers and the membrane is called a composite. Composite membranes have the advantage of each layer being individually optimized—the skin for its permeability and the support for its strength—but they are harder to make them integral membranes.

Polyelectrolytes, except those which are covalently cross-linked, are soluble in water, and their applications are based on this property. Basically, these applications depend on the polyelectrolyte altering the fluid properties of an aqueous medium, or modifying the behavior of particles in aqueous slurries or colloidal suspensions.

Polyelectrolytes raise the viscosity of aqueous solutions thus acting as thickeners, and the magnitude of the effect increases with the polymer's molecular weight. Naturally occurring gums

and acidic polysaccharides have been traditionally used as thickening agents in food stuffs and pharmaceutical products, but, more recently, synthetic polyelectrolytes have been used in these roles. Much use is also made of polyelectrolytes to modify the characteristics of latex paints and similar proprietary fluids.

Polyelectrolytes can also stabilize particles in aqueous suspension and so act as dispersants. In this reaction, the hydrophobic backbones of polyelectrolytes are absorbed onto the surface of the particles by van der Waals attraction, while their ions form a hydrophilic surface and interacts with water. In suspension or bead polymerization, for example, a hydrophobic vinyl monomer is dispersed in water by agitation to form droplets that are stabilized by a polyelectrolyte. Each stabilized droplet of the monomer acts as a bulk polymerization system and on polymerization gets the shape of a bead.

Polyelectrolytes, depending on their ionic charge, can interact with colloidal particles and neutralize the stabilizing hydrophilic charges, thus acting as flocculating agents. They have been used in this way to coagulate slurries and industrial wastes.

There are other applications of polyelectrolytes that depend on their behavior in water in various ways. They are thus used as sizes in the textile industry and in paper manufacturing, and as additives to drilling muds and to soil for conditioning purposes.

A very different kind of application of polyelectrolytes is their use as dental cements. Here a divalent cation is added to an aqueous solution of a polyanion to form a highly cross-linked precipitate of great strength.

5.10.2 Ionomers

5.10.2.1 Polyethylene Ionomers

Ionomers based on polyethylene were described earlier ([Chapter 4](#)). They are mainly copolymers with pendant carboxylate groups in which the polyethylene backbone is their major component (>90%). Ethylene is directly copolymerized with methacrylic acid in a continuous process developed from the high-pressure method used to make low-density polyethylene by free-radical initiation. The comonomers are mixed in appropriate proportions, allowing for the greater reactivity of the methacrylic acid, and introduced with a peroxide initiator to a reactor at a pressure of about 30,000 psi (207 MPa) and a temperature of 250–280°C. Because methacrylic acid reacts disproportionately rapidly and has to be replenished frequently, the conversion to polymer is kept low per pass, and at 15–20% conversion the residual monomer is removed, then recycled with fresh monomer. This ensures that the methacrylic acid units, and hence the ionic cross-links formed later, are randomly distributed and uniform in composition.

The distinctive properties of the ionomers become manifest only when the carboxylic acid groups are neutralized. The neutralization is a kind of post-treatment that is performed by melting the polyacid in a mill at 150°C and adding a base or basic salt in powder form or in solution. In these neutralizations, the melt starts as a soft, fluid, opaque mass of polyacid and then becomes stiff, rubbery, and transparent as the ionomer is formed.

The loss in fluidity, or gain in melt strength, is a significant factor determining the usefulness of ionomers. That the effect is due to the formation of strong ionic cross-links is clearly shown by a comparison of the melt viscosity of an ionomer with its acid precursor ([Figure 5.59](#)). The melt viscosity of a copolymer of ethylene and methacrylic acid containing, for example, 2 mole per cent of acid is increased by only about 50% compared to an otherwise equivalent polyethylene homopolymer, but when neutralized, and therefore ionized, the melt viscosity increases twenty-fold. (The slight increase with the acid is attributed to the weak hydrogen-bonded cross-links.) The melt-strength of an ionomer is such that its molten film can be drawn over the sharp edges of a nail without it being punctured or torn.

Though, as just explained, the viscosity of an ionomer at low shear is very much greater than its acid precursor, at high shear, however, the two are nearly the same ([Figure 5.60](#)), which is attributed to breaking down of the physical bonding of the cross-links. The high shear sensitivity of melt viscosity is an important characteristic of ionomers and is a useful feature in a number of melt-fabrication processes.

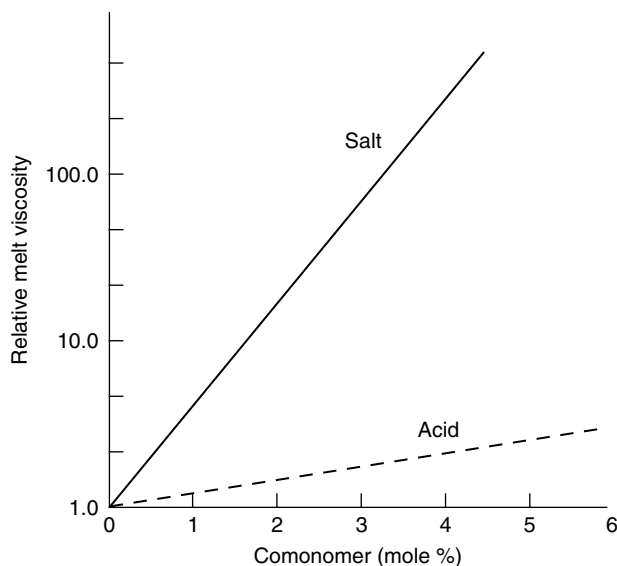


FIGURE 5.59 Melt viscosity of poly(ethylene-co-methacrylic acid) and its sodium salt relative to polyethylene.

Thus the high melt-strength at low shear makes ionomers useful for extrusion or blow-molding, or for any process where the melt is partially supported.

A striking property of the ethylene ionomers is that they are transparent, unlike their acid precursors or polyethylene itself, which are not. The haze in polyethylene is due to the fact that the polymer is partially crystalline, and minute crystallites within it agglomerate into spherulites, which are of a size to scatter light. Ionomers also contain crystallites, and the crystallite formation is, in fact, helped by the ions, the domains of which serve to nucleate them; but the crystallites are unable to agglomerate because of the high viscosity of their surroundings. Thus, microcrystallinity is enhanced by the ions, but macrocrystallinity, which causes haze, is inhibited. The transparency of ionomers is useful in packaging applications.

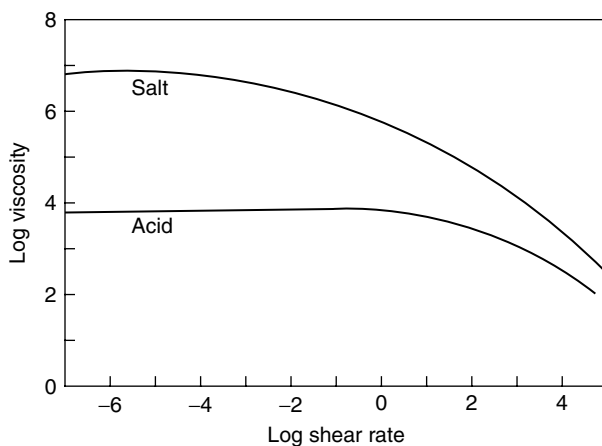


FIGURE 5.60 Melt viscosities (160°C) at various shear rates of poly(ethylene-co-methacrylic acid) with 3.5 mole% comonomer and its sodium salt.

Some physical properties of polyethylene ionomers are compared with those of polyethylene and the acid copolymer, poly(ethylene-co-methacrylic acid) in Table 5.15. Ionomer is generally tougher and, as shown in Table 5.15, relative to the acid copolymer, its tensile strength is increased by 27–53% and its stiffness is nearly tripled.

Polyethylene ionomers are described as flexible and tough with good impact toughness at low temperature, and with good resistance to grease and solvents, to stress-cracking, and to abrasion. They are blow-molded into films, sheets, bottles, and blister packs, and injection-molded into various objects. Their resistance to grease and solvents has made them useful in meat packaging. They are very effective as external coatings on glass bottles to contain breakages.

5.10.2.2 Elastomeric Ionomers

A number of ionic polymers exist that have a recognized elastomer as the covalent backbone and have a small ionic content, so they may be called elastomeric ionomers. The ions provide at least a part of the cross-links in these polymers. Those elastic ionomers that are cross-linked exclusively by their ions have, however, the useful feature of being thermoplastic.

Carboxylated polybutadiene ionomers, which are close relatives of the polyethylene ionomers described above, have an essentially polybutadiene backbone that contains some acrylonitrile and styrene to adjust its flexibility and toughness, and, in addition, up to 6% by weight of acrylic or methacrylic acid. Like the polyethylene ionomers, they are usually made by direct copolymerization with the carboxylic acid monomer using, however, emulsion methods. Typically the monomers are slurried in water with sodium dodecylbenzene sulfonate as the emulsifier and potassium persulfate as the free-radical initiator. The tendency of the carboxylic acid monomer to dissolve in the aqueous phase instead of remaining in the butadiene-rich phase is suppressed by making the aqueous phase acidic so that the monomer remains in the nonionized form.

The carboxylated polybutadienes, when neutralized, undergo ionic cross-linking, producing the effect of vulcanization. The neutralization can be done by treating with aqueous sodium hydroxide then heating, or by heating directly with zinc oxide. The ionic cross-link formed with the sodium ion of moderate strength at room temperature and dissociates at 100°C. With zinc, the ionic cross-link formed is much stronger, although the polymer is capable of substantial flow at higher temperatures.

Some properties of sodium and zinc vulcanizates are compared with those of the acid precursor in Table 5.16. High tensile strength is a characteristic of ionic vulcanizates. As a comparison, a standard polybutadiene elastomer vulcanized with sulfur gives a strength of 1.9–5.8 MPa (275–841 lbf/in.²), whereas an equivalent copolymer containing 1.5 mole% methacrylic acid, and vulcanized with

TABLE 5.15 Comparative Physical Properties of Polyethylene Ionomers and Their Acid Precursor

Property	PE	Copolymer ^a (–CO ₂ H)	Ionomer	
			Na ⁺	Zn ²⁺
Appearance	Hazy	Hazy	Transparent	Transparent
Melt index (g/10 min) ^b		5.8	0.03	0.09
Yield strength (10 ³ lbf/in ²)	1.20	0.88	1.91	1.93
(MPa)	8.3	6.1	13.2	13.3
Elongation (%)	600	553	330	313
Tensile strength (10 ⁶ lbf/in ²)	1.8	3.4	5.2	4.3
(MPa)	12.4	23.4	35.9	29.6
Stiffness (relative)		1.0	2.8	3.0

^a Poly(ethylene-co-methacrylic acid) with 3.5 mole% methacrylic acid comonomer.

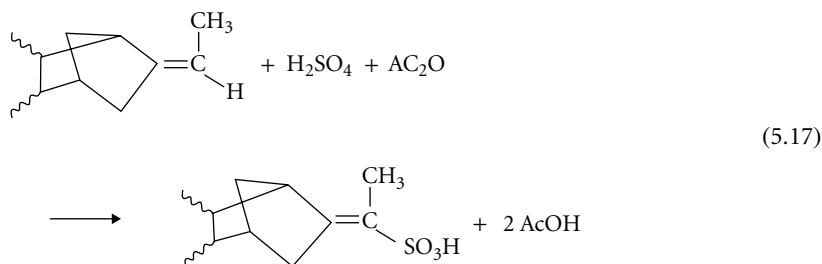
^b ASTM-D-1238-57T.

magnesium oxide, gives 29.0 MPa (4.2×10^3 lbf/in.²). They also respond differently to fillers such as carbon black—sulfur vulcanizates are reinforced, while ionic vulcanizates are weakened.

Carboxylated polybutadienes have not been used much as thermoplastic elastomers, principally because they have poor compression set, high stress relaxation, and poor performance at higher temperatures. Carboxylated polybutadienes, supplied as lattices, are used mainly in dipping and coating processes, applications, which often do not involve ionized carboxylate, at least directly. The applications include adhesives, paper coating, glove-dipping, carpet-backing, binding nonwoven fabrics, and also shrink-proofing woolen garments where the carboxyl groups are believed to react with pendant amino groups in the proteins of the wool. A wide range of carboxylated lattices are available as well-developed items of commerce; some of these are styrene-butadiene rubbers (SBRs) and others are acrylonitrile-butadiene rubbers (NBRs).

Mixed vulcanizations, such as with zinc oxide and sulfur or zinc oxide and peroxide, are used for carboxylated NBRs in order to combine the advantages of the ionic method with the conventional methods. The mixed vulcanizates have high tensile strength and notable resistance to abrasion, oil, and fuel. They are used in applications such as industrial rollers and wheels and shoe soles. Dry NBRs are available in fewer grades than lattices. Examples are Krynac by Doverstrand and Hycar by Goodrich.

Elastomeric ionomers have also been developed from ethylene-propylene-diene ternary copolymers known as EPDM rubbers. The diene is commonly ethylidene norbornene. Du Pont made carboxylated ionomers by free-radical grafting of maleic anhydride (0.5–5%) onto the diene moiety of the polymer and neutralized the product with rosin salt. The ethylidene norbornene can also be sulfonated, thus:



Ionomer properties of sulfonated EPDM are said to develop only when the acids are neutralized. The best properties are given by zinc salts, particularly when they are plasticized by zinc stearate. (See the section on [thermoplastic elastomers](#) in [Chapter 4](#) for properties of ionic elastomers.)

5.10.2.3 Ionomers Based on Polytetrafluoroethylene

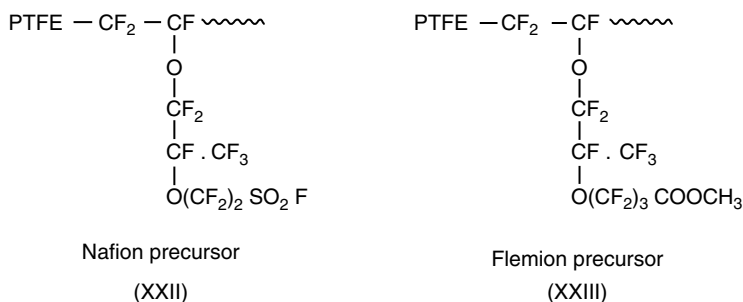
Polymers with a polytetrafluoroethylene (PTFE) backbone and pendant perfluorosulfonate or perfluorocarboxylate groups have become commercially important materials, although they are expensive. The sulfonates were introduced as Nafion by Du Pont in the early 1970s and the carboxylates as Flemion by Asahi Glass in 1978. They are made by free-radical copolymerization of tetrafluoroethylene and perfluorovinyl monomers giving precursor copolymers, (XXII) and (XXIII), which can be post-functionalized by hydrolysis to generate sulfonic and carboxylic acid groups. The perfluorovinyl

TABLE 5.16 Vulcanization of Carboxylated Polybutadienes

Form	Tensile Strength		Elongation (%)
	10^3 lbf/in. ²	MPa	
Acid copolymer	0.1	0.7	1600
Sodium vulcanizate	1.7	11.7	900
Zinc vulcanizate	6.0	41.4	400

Poly(butadiene-co-methacrylic acid) with 6.7 mole% methacrylic acid.

monomers themselves are made from tetrafluoroethylene by multi-step synthesis using hexafluoropropylene oxide.



Although originally developed for use as a membrane in fuel cells, Nafion has found more useful applications in various other electrolytic separation processes. In these applications, use is made of its cation-exchange properties and its ability to survive in extremely aggressive chemical environments. An outstanding example is the use of Nafion as a membrane in the chlor-alkali cell where it is gradually replacing the traditional diaphragm and mercury cells. In the chlor-alkali process a cell is partitioned by the polyanionic membrane into an anode compartment, to which brine is added, and a cathode compartment to which water is added (Figure 5.61). On application of electric potential, Na^+ passes from the brine around the anode and through the membrane to the water around the cathode where it forms sodium hydroxide. The membrane keeping the brine and water separate allows transfer of Na^+ ions by ion-exchange and acts as a barrier to Cl^- and OH^- .

The Nafion membranes have ionic contents of 0.66–0.91 Eq/kg. A bilayer of these two extremes of composition is made and also a bilayer with a perfluorocarboxylate (Flemion) polymer. The bilayered membranes are made by melt processing the precursor copolymer, which then, in membrane form, is hydrolyzed.

Perfluorocarboxylates, the Flemions, were introduced with the idea that a carboxylate at a given ion content would be less hydrophilic than a sulfonate and so would be of help in balancing the ionic content of an ion-exchange membrane with its permselectivity and hydrophilicity as required. The bilayered Nafions also resulted from similar thinking and at tempt to combine certain advantages of the two types.

The efficiency with which power is consumed in the electrolysis and the highest concentration of uncontaminated sodium hydroxide that can be produced determine the membrane performance in the

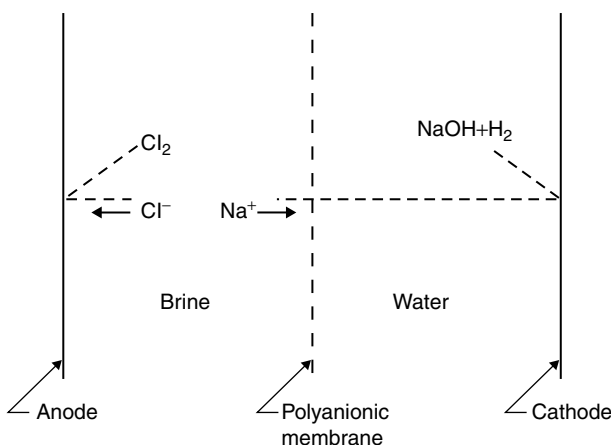
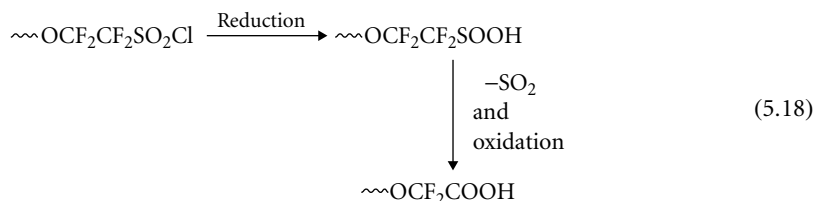


FIGURE 5.61 Chlor-alkali cell.

chlor-alkali process. Rapid progress in membrane performance has been made since the introduction of carboxylate membranes, leading to an efficiency level of 95% and a concentration of 33%.

Bilayer carboxylate membranes can be produced by surface modification of Nafion-type membranes. In a process used by Asahi Chemical the sulfonate on a Nafion-type surface is reduced to sulfinic and sulfenic acids, then oxidized to a carboxylate layer of 2–10 μm thickness:



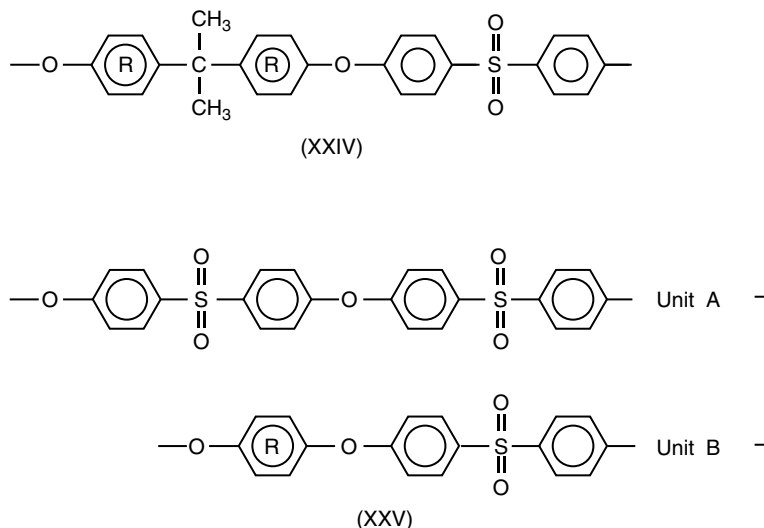
Tokoyama Soda makes Neosepta F membranes by treating a Nafion-type precursor with an alcohol and the oxidizing the surface in air.

Nafions in their acid forms are super-acidic, i.e., stronger than sulfuric acid and so have high catalytic power. Nafion powders in acid form have therefore been used as catalysts in many types of reactions, such as esterification and Friedel-Crafts reactions at low temperatures.

5.10.2.4 Ionomers Based on Polysulfones

Ionomers of commercial polysulfones, principally sulfonates, are being developed as membranes, particularly for purifying water by reverse osmosis. In this application, they are superior to conventional membrane materials because they are resistant to oxidation by the chlorine used in water treatment, to harsh chemical cleaning operations, to biological fouling, and to compaction under high operating pressures. The traditional polymer, cellulose acetate, is less strong, while Nafion, though very inert chemically, is too costly and difficult to fabricate in a form suitable for reverse osmosis. The sulfones, having completely amorphous backbones and solubility, can be easily cast into membranes from solvents. The optimum ion content is about one eq/kg, which provides a balance of properties between a high flux of the permeant (water) and a low leakage of the rejected species (the dissolved salts).

Commercial polysulfones (see Table 4.30) such as Udel (Union Carbide) and Victrex (ICI) are sulfonated in a post-functionalization step to make ionomers. When dissolved in dichloroethane and treated with a complex of sulfur trioxide and triethyl phosphate, Udel (XXIV) becomes monosulfonated on the rings marked **R** (as the rings connected to the sulfone group are deactivated by the sulfone group).



Victrix is a random copolymer of two units (XXV) in which the ring marked **R** of unit **B** becomes monosulfonated by the simple process of dissolving it in sulfuric acid. The other aromatic rings and the whole of unit **A** are inert. The extent of the reaction is predetermined by the proportion of unit **B** in the copolymer. The strength of the ionic associations in sulfonated Victrix is indicated by the increase in T_g , which occurs linearly with the content of unit **B** despite the already high value of 230°C for the parent polymer.

5.10.3 Polyelectrolytes

5.10.3.1 Ion-Exchangers

The most important class of ion-exchangers are the organic ion-exchange resins. Their framework, the so-called matrix, consists of an irregular, macromolecular, three-dimensional network of hydrocarbon chains. The matrix carries ionic groups such as $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$, and AsO_3^{2-} in cation exchangers and $-\text{NH}_3^+$, $-\text{NH}_2^+$, $-\text{N}^+$, and $-\text{S}^+$ in anion exchangers. Ion-exchange resins thus are cross-linked polyelectrolytes. The first completely synthetic ion-exchange resins were prepared by B. A. Adams and E. C. Holmes in England in 1935. Today more than 100 synthetic ion-exchange resins are marketed throughout the world by various companies. Some of the largest manufacturing companies and the trade names of the resins are listed in Table 5.17.

Ion-exchange resins are supplied as insoluble, water-swelling beads that have either a dense internal structure (gel-type) or a porous, multichannelled one (macroporous-type or macroreticular). The gel-type PS resin was the first to be introduced (1947) and the macroporous-type came later (1959).

Ion-exchangers are broadly classified as cation exchangers and anion-exchangers. Carriers of exchangeable cations are called cation exchangers; they have acidic functional groups bound to the resin matrix. Carriers of exchangeable anions are called anion exchangers; they have basic functional groups bound to the resin matrix (Table 5.18). Chelating ionexchange resins contain chemically bound chelating functional groups, which sorb metal ions by chelation.

Polystyrene (PS) cross-linked with divinyl benzene (DVB) is the matrix on which most of the commercial ion-exchange resins are based; the ionic groups are introduced by post-functionalization of the cross-linked polymer matrix. By varying the DVB content, the degree of cross-linking can be adjusted in a simple and reproducible manner. The nominal DVB content, which refers to mole% of DVB in the polymerization mixture, is used to indicate the degree of cross-linking. General-purpose ion-exchangers contain between 8 and 12 mole% DVB, the most common being 8 mole%. For special purposes, resins with as little as 0.25% DVB and as much as 25% DVB have been prepared. Resins with low DVB content swell strongly and are soft and gelatinous, while those with very high DVB content swell very little and are tough and mechanically more stable.

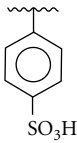
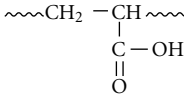
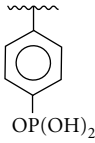
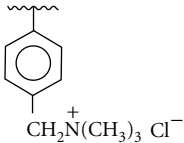

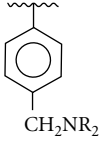
TABLE 5.17 Trade Names and Manufacturers of Ion-Exchange Resins

Trade Name	Manufacturer
Amberlite	Rohm and Haas Co., Philadelphia, PA
De-Acidite	The Permutit Co. Ltd., London, England
Dowex	Dow Chemical Co., Midland, MI
Duolite	Chemical Process Co., Redwood City, CA
Imac	Industriele Mij. Activit N. V., Amsterdam, Netherlands
Ionac ^a	Ionac Co. Ltd., New York, NY
Lewatit	Farbenfabriken Bayer, Leverkusen, Germany
Nalcite ^b	National Aluminate Corp., Chicago, IL
Permutit	Permutit Co., New York, NY
Wofatit	VEB Farbenfabrik Wolfen, Wolfen, Kr. Bitterfeld, Germany
Zeo-Karb	The Permutit Co. Ltd., London, England

^a Product of Permutit Co., marketed by Ionac Co.

^b Product of Dow chemical Co., marketed by National Aluminate Corp.

TABLE 5.18 Types of Ion-Exchange Resins

Active Group	Structure
<i>Cation-exchange resins</i>	
Sulfonic acid	
Carboxylic acid	
Phosphonic acid	
<i>Anion-exchange resins</i>	
Quaternary ammonium salt	
Secondary amine	
Tertiary amine	

The styrene-DVB copolymer beads are prepared by suspension (pearl) polymerization technique. The monomers are mixed and a polymerization catalyst such as benzoyl peroxide is added. The mixture is then dispersed into small droplets in a thoroughly agitated aqueous solution that is kept at a temperature required for polymerization (usually 85°C–100°C). A suspension stabilizer (gelatin, polyvinyl alcohol, sodium oleate, magnesium silicate, etc.) in the aqueous phase prevents agglomeration of the droplets. The size of the droplets depends chiefly on the stabilizer, the viscosity of the solution, and the agitation, and it can be varied within wide limits. As polymerization takes place, the droplets are transformed into polymer beads. For most purposes, a bead size of 0.1–0.5 mm is preferred, but beads from 1 μm to 2 mm in diameter can be prepared without much difficulty.

The above method gives beads of gel-type polymer matrix. Porous beads can be made by incorporating a component (for example, styrene homopolymer) that is soluble in the monomer mixture. After polymerization this component is removed from the matrix with, for example, toluene, thus leaving pores within the structure in the final product.

Highly porous, so-called macroreticular beads can be prepared by a variation of the conventional pearl polymerization technique. An organic solvent is added in which the mixture of monomers is soluble, but the polymer, when it is formed, is insoluble. Thus, as polymerization progresses, the solvent is squeezed out by the growing polymer regions. In this way, one can obtain spherical beads with large pores (several hundred angstrom units), which guarantee access to the interior of the beads even when nonpolar solvents are used.

Styrene-DVB copolymer beads are sulfonated to produce the most widely used strong-acid type cation-exchange resins. To make them, the copolymer precursor beads are dispersed in about 10 times their weight of concentrated sulfuric acid and heated slowly to 150°C. The sulfonic acid group is normally introduced into the para position. Though the reaction is very simple in principle, it involves delicate operations and close control of parameters in order to achieve beads of suitable structure and durability. A fully mono-sulfonated, polystyrene has a theoretical ion content of 5.1 equivalents/kg (dry) but many commercial resins have about 4.4–5.2 eq/kg. Amberlite IR-120, Dowex-50, Nalcite HCR, Permutit Q, Duolite C-20 and C-25, and Lewatit S-100 are resins of this type.

Weak-acid, cation exchange resins are prepared by copolymerization of an organic acid or acid anhydride and a cross-linking agent. As a rule, acrylic or methacrylic acid is used in combination with divinyl benzene, ethylene dimethacrylate, or similar compounds with at least two vinyl groups. The pearl polymerization technique described above can be used if esters instead of the water-soluble acids are polymerized. The esters are hydrolyzed after polymerization. The final products have ionic contents of 9–10 eq/kg (dry). Resins of this type are Amberlite IRC-50, Duolite CS-101, Permutit H-70, and Wofatit CP-300.

Strong-based anion-exchange resins, also very common, are made (Figure 5.62) by chloromethylating the styrene-DVB copolymer, then aminating the product with a tertiary alkyl amine. The quaternization of chloromethylated resins with tertiary alkyl amines takes place smoothly and quantitatively. The two most common strong-base resins are made with trimethylamine and contain the quaternary amine groups— $\text{N}(\text{CH}_3)_3$ and— $\text{N}(\text{CH}_3)_2\text{CH}_2\text{OH}$. The first type of resin is classed as a Type I strongbased anion exchanger and the second type as a Type II exchanger. Dowex-1, Amberlite IRA-400, Permutit S-1, Nalcite SBR, Duolite A-42, and De Acidite FF are Type 1 resins. Dowex-2, Amberlite IRA-410, Permutit S-2, Nalcite SA-R, and Duolite A-40 are Type II resins. The resins Amberlite IRA-401 and 411 differ from

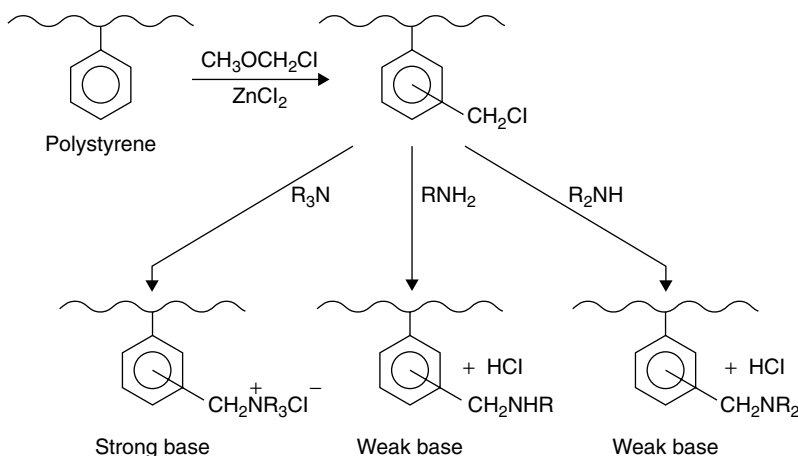
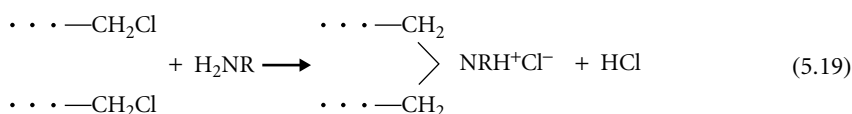


FIGURE 5.62 Reaction scheme for the preparation of weak-base and strong-base resins starting with polystyrene.

the standard types 400 and 410 only by having a lower DVB content. The ion contents of strong-based resins are 3–4 eq/kg (dry).

Type I resins have better thermal and oxidative stability and maintain the integrity of the quaternary groups over a long period of time. Type II resins, when used in the hydroxide form, are limited to a maximum temperature of approximately 40°C and should not be used under oxidizing conditions. Type II resins are often used because of lower operations costs. They regenerate somewhat more easily and have higher operating capacities than the Type I products. The resins have a useful industrial life of 3–5 years.

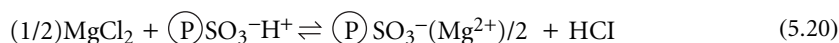
Weak-base resins are made by treating a chloromethylated intermediate with primary or secondary alkyl amines (Figure 5.62). The treatment with secondary amines leads to monofunctional weak-base resins having tertiary amino groups. By treatment with primary alkyl amines, however, polyfunctional weak-base resins having secondary and tertiary amino groups are obtained, the latter being formed by the reaction of the primary amine with two chloromethyl groups:



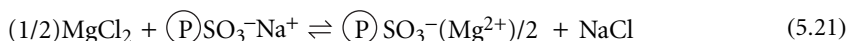
Additional cross-linking results if the chloromethyl groups belong to different chains (Occasionally, polyamines such as tetramethylenepentamine are used; they can react in a similar way with two or more chloromethyl groups.) The resins Amberlite IR-45, Dowex-3, Nalcite WBR, and Duolite A-14 are polyfunctional weak-base anion exchangers. De-Acidite G is a monofunctional resin with tertiary amino groups.

Deionization by ion-exchange is usually confined to relatively dilute solutions, i.e., concentrations less than 0.03N (1500 ppm CaCO_3). Since ion-exchange resins have finite capacities, economics are most favorable for dilute solutions, although concentrations up to 0.1N (5000 ppm CaCO_3) can be treated quite satisfactorily.

Cation exchange resins having strongly acidic sulfonic acid groups are the major cation exchangers used for deionization purposes. When dilute solutions are passed through beds of such resins, either in acid form or sodium salt form, cation exchange takes place according to the following reactions (shown for MgCl_2):



or



The above reactions are reversible, and the exhausted resin can be regenerated with moderate concentrations of strong acids or NaCl. The relative affinities for the resin of various cations have an important influence on the efficiency of exchange. In general, the order of ease of replacement of common cations is $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Al}^{3+} > \text{Fe}^{3+}$.

Strongly basic anion-exchange resins can act as acid neutralizers or can split salts in the same manner as the sulfonic acid cation exchangers. The following are typical reactions:



or



The resins show marked affinity relationships depending on ion size and valence. The order of affinity for common anions is: $\text{SO}_4 > \text{Cl}^- > \text{HCO}_3^- > \text{F}^- > \text{HSiO}_3^-$. Reaction (23) can be reversed by

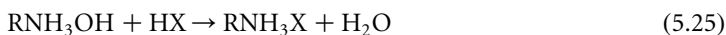
regenerating with moderate concentrations of sodium hydroxide solutions. However, since the reactions are not as easily reversed, regeneration levels of 150%–200% of the stoichiometric requirements are frequently employed.

In addition to the commonly employed sulfonic acid cation exchanger, resins based on the carboxylic acid groups are sometimes employed under special conditions. These resins are effective for exchange reactions in neutral and alkaline solution. For example, the effluent from a saltsplitting reaction, Equation 5.23, can be treated with a carboxylic exchanger according to the reaction:



The reaction is reversed very effectively by the hydrogen ion, and regeneration can be accomplished readily at efficiencies approaching 100%.

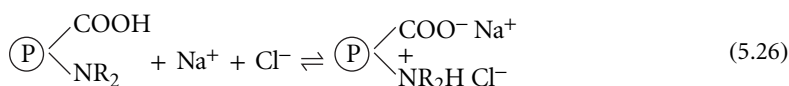
The role of weak-base anion-exchange resins in deionization is often confined to acid neutralization, as shown by the following equation:



The reaction can be reversed by addition of some alkaline reagent such as NaOH, Na₂CO₃, NH₃, and NaHCO₃. The regeneration is accomplished readily at efficiencies approaching 100%. The ease with which the hydroxyl ion can be replaced by other anions is SO₄²⁻ > Br⁻ > F⁻ > CH₃COO⁻ > HCO₃⁻.

The weak-acid and weak-base resins do not totally demineralize the water like their strong counterparts. However, the water they produce, containing 100–200 ppm of dissolved solids, is adequate for many purposes. The regeneration of the weak resins is also accomplished more readily than the strong resins.

A relatively recent development is a thermally regenerable ampholytic resin containing both weak acid and a weak-base functionality within the one bead (Sirotherm by ICI), which absorbs significant quantities of salt at ambient temperatures and releases salt on heating to 70–90°C. Thus, when the resin is fully exchanged or exhausted, it can be rinsed in hot water and reused. The adsorption step involves the transfer of protons from carboxylic acid groups to amino groups to form the cation and anion exchange sites:

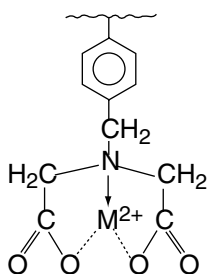


The equilibrium is temperature sensitive, with both types of groups showing weaker electrolyte behavior on heating. The large increase in the ionization of water that occurs on heating, about 30-fold from 25°C to 85°C, releases additional protons and hydroxyl ions, which suppress the ionization of the weak electrolyte resins. The hot water can thus be looked on as providing the acidic and basic regenerants that usually have to be added separately.

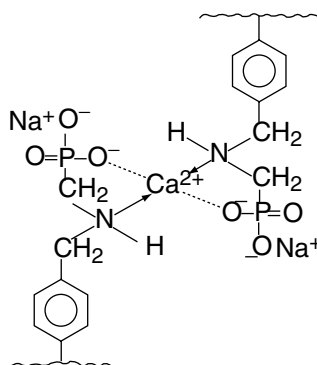
Operating data indicate that Sirotherm TR-20 resins can produce waters of salinities as low as 50–100 ppm dissolved salts, the economic upper range of salinities in feed water being restricted to 2000–3000 ppm. The resins are expected to find application in the demineralization of mildly brackish surface and underground waters for industrial and municipal use and as a roughing stage in the production of high-quality boiler feed water.

Some polystyrene resins (cross-linked with DVB) are specially modified to have chelating functional groups bound to the matrix so as to make them selective towards certain ions. Such resins with iminodiacetic acid groups are marketed under the trade names Dowex A-1 (Dow Chemical) and Chelex 100 (Bio-Rad Laboratories). The complex (XXVI) formation constants with metal ions of the chelating resin are so large that the resin absorbs metal ions equivalent to the iminodiacetic acid groups (used in sodium salt form), i.e., the efficiency of metal ion adsorption is near 100%. A particular metal ion can be removed by controlling the pH of aqueous solution. For example, at pH 2, mercury and copper ions are

preferentially adsorbed, while zinc, cobalt, and cadmium ions are little adsorbed.



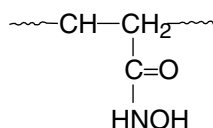
(XXVI)



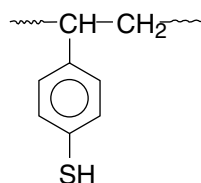
(XXVII)

Polystyrene resins that have aminophosphonate chelating groups are highly selective towards calcium ion. Such a resin, e.g., Duolite ES467 (Rohm and Haas), when added to a strong brine solution (25%) contaminated with 10 mg/liter of calcium ion will selectively remove the calcium ion, forming calcium amino-phosphonate complex (XXVII), until only 0.02 mg/liter remains. This process is particularly useful for purifying the brine used in the chlor-alkali cell described earlier.

Many other specific resins have been prepared. To give only a few examples, resins with hydroxamic acid groups (XXVIII) are specific for Fe^{3+} ions and those with mercapto groups (XXIX) prefer Hg^{2+} ions. Resins containing chlorophyll and haemin derivatives or similar compounds form extremely strong chelates with ions such as Fe^{3+} . In fact, the chelated counterions are held so strongly that they can hardly be displaced. Another undesired consequence of such strong association is that the mobility of the counterion in the resin is greatly reduced. Hence for any application one should choose the resin carefully, seeking a reasonable compromise between selectivity, ease of regeneration, and rate of ion exchange.



(XXVIII)



(XXIX)

Prior to the development of polystyrene resins, phenol-formaldehyde (P-F) condensates were used as matrices, but they have now been replaced. A few weak-base types still exist (e.g., Duolite ES562 of Rohm and Haas), which are made by adding an amine during polycondensation. These P-F condensates are used for enzyme fixation.

5.10.3.2 Applications

Applications of ion-exchange resins are extremely varied, ranging from water-softening to purification of chemicals and therapeutic applications. An extremely useful industrial development of the ion-exchange technique is the production of demineralized water rivaling that of distilled water in purity.

Most ion-exchange reactions for industrial applications are done with columns of resin in which the ions in solution (say B) are depleted, proceeding from top to the bottom of the column, by exchange with ions (say A) in the resin. With the progress of ion exchange the resin bed shows an exhausted portion at the top, an ion-exchange zone in the middle and a regenerated portion at the bottom (Figure 5.63).

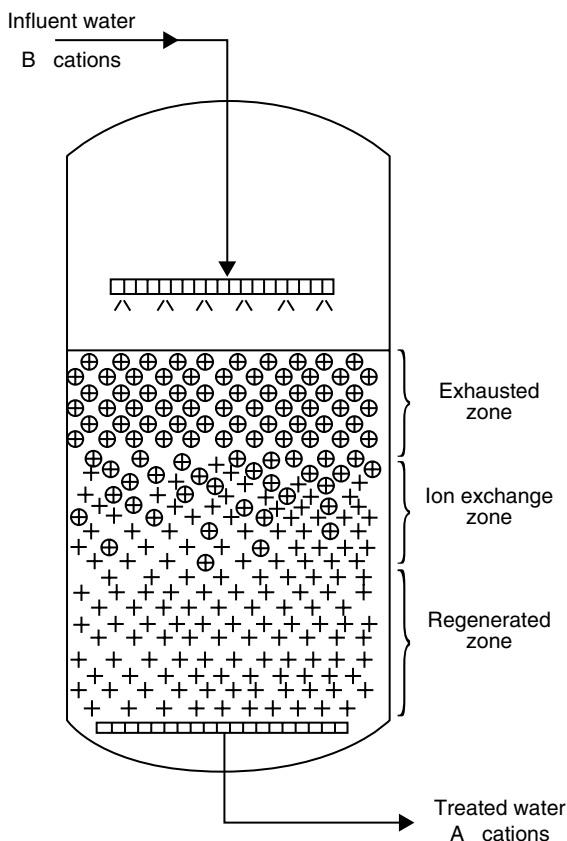


FIGURE 5.63 Ion-exchange column in service: (+, resin containing A cations; \oplus , resin containing B cations).

As the ion-exchange zone moves down through the resin column, the **B** ions eventually reach the outlet, at which time breakthrough occurs.

In most ion-exchange installations, the vertical column is the most commonly employed unit. The system may consist of a single column with one type of resin (single column system), two or more columns containing a variety of cation and/or anion exchange resins (multiple-bed system), or a single column containing a mixed bed of two (or more) resins (monobed or mixed-bed system).

Much of the appeal of the ion-exchange process stems from the simplicity of the single-column system. Water softening by ion-exchange is the most widely used example of this system (Figure 5.64). The hardness ions, calcium and magnesium, are exchanged for sodium as the hard water flows down through a column of cation exchange resin used in the sodium form [see Equation 5.21]. Conversion of the exhausted resin back to the sodium form [i.e., reverse of Equation 5.21] is accomplished in a regeneration step by contacting the column with an excess of sodium chloride solution. Water softeners range in size from small household units (e.g., 20 cm in diameter and 60 cm deep) to large industrial units (e.g., 360 cm in diameter and 150 cm deep).

It will be noted that in reactions (20) and (22) the overall result of ion-exchange is the complete elimination of dissolved salts with the formation of an amount of water equivalent to the amount of electrolyte removed. Deionization requires contacting the water with both cation and anion exchange resins, which can be done in a multiple-bed system.

Two-bed deionization of water is widely practiced. Such systems generally use a strong-acid cation exchange followed by either a weak-base or a strong-base anion exchanger. Reactions similar to equations

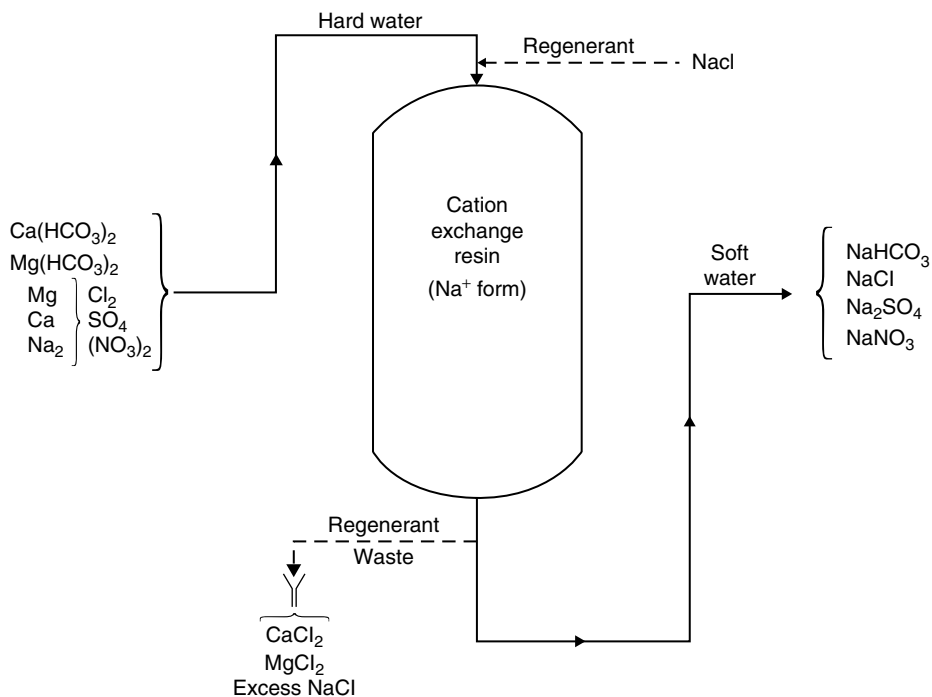
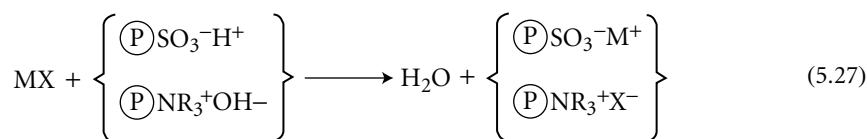


FIGURE 5.64 Water softening by ion-exchange in single-column system.

(20), (22), or (25) occur. Three beds or more are used either to achieve operating economy or a greater degree of deionization. For example, a three-bed system of strong acid cation exchanger/weak-base anion exchanger/strong-base anion exchanger offers economy in regeneration. In service, the weak-base resin removes the mineral acids coming from the cation exchanger and the strong-base resin removes principally carbonic and silicic acids.

For installations requiring very high effluent water quality, monobed or mixed-bed deionization has been used widely, yielding a demineralized water in one operation. The standard mixed-bed is a special case of a single column. It usually consists of an intimate mixture of a strong-acid cation exchange resin and a strong-base anion exchange resin in the hydrogen and hydroxide forms, respectively. When water is passed through a fixed bed of such a mixture, the ions in solution are alternately exposed to numerous contacts with cation and anion exchange sites, the effect being similar to that obtained with a very large number of multiple beds, with the result that almost complete deionization occurs. The process follows the reaction:



Following exhaustion of a mixed bed and prior to regeneration, the resins in the bed are separated by applying backwash at a flow rate sufficiently high to fluidize the bed. By virtue of that fact that anion exchange resins have a lower density than cation exchange resins, hydraulic separation into two layers occurs. The regenerant caustic soda then contacts the upper layer of anion resin and the acid regenerant

flows through the lower layer of cation resin. Then following a rinse with relatively pure water, the resins are air-mixed prior to the next ion-exchange run.

Ion-exchange methods are established for treating various effluents arising from the metal finishing processes such as plating and anodizing. The use of strong-base resins for decolorizing sugar liquors is widely practiced. The coloring bodies are organic anions that are sorbed by weakly cross-linked strong-base gel resins.

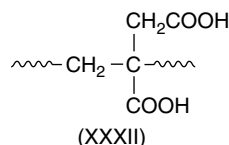
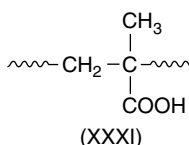
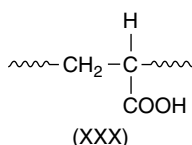
Even wines are sometimes treated by column cation exchange. Potassium hydrogen tartrate, which causes an unpleasant precipitate in wines, is converted to the more soluble sodium salt by treatment with polystyrene sulfonic acid resin in the sodium (Na^+) form.

Ion-exchange resins are used for metal recovery from low-grade ores and dilute leach liquors. One of the best examples is the recovery of uranium.

Ion-exchange chromatography is well known for separating mixtures of ions in solution. Possibly the best-known organic analytical ion-exchange application is the chromatographic separation and isolation of amino acids. Commercially, the most significant application is the recovery of antibiotics such as streptomycin and neomycin. The fermentation broth containing the impure antibiotic is treated with a polyacrylic weak-acid resin on which the antibiotic is sorbed to the exclusion of other organic impurities. The product is recovered by elution with dilute mineral acid.

5.10.3.3 Polycarboxylates

Polyacrylate-type homopolymers are polyelectrolytes and are the most ionic of the organic polymers. They dissolve in water giving aqueous solutions with unusual and useful physical properties. They are generally made by free-radical polymerization in aqueous solution. Very-high-molecular weight (e.g., 4×10^6) polymers can be obtained that give very viscous solutions. Polyacrylic (XXX), polymethacrylic (XXXI), and polyitaconic (XXXII) acids are the three main types having theoretical capacities of 13.9, 11.6, and 15.4 eq/kg, respectively. Aqueous solutions or dry powders of these materials are commercially available.



Versicols (Allied Colloids) and Texigels (Scott Bader) are homopolymers of acrylic or methacrylic acids or their copolymers with acrylamide. They are used as stabilizers, and protective colloids and thickeners for aqueous dispersions, binders, and flocculants. Carbopols (B. F. Goodrich) are different grades of polyacrylic acid of varied molecular weight having excellent suspending, thickening, and gel-forming properties. CarboSETS (B. F. Goodrich) are acrylic copolymers and have a similar carboxylic content but generally can be dissolved in alkaline solutions. They are used mainly in coating applications. In some applications, they are covalently cross-linked with epoxides and so on, but some applications use ionic cross-links made with zinc ions.

A notable application of polyacrylic acid is for cements in dentistry. These are made by mixing an aqueous solution of the polymer with zinc oxide when the zinc salt precipitates as a highly cross-linked gel that rapidly sets to a hard mass under oral conditions. In a variation of this reaction, the zinc oxide is replaced with a tooth-colored glass powder that releases Al^{3+} and Ca^{2+} ions. These cements, called ASPA (aluminosilicate polyacrylic acid) or glass ionomer, set very rapidly, bond well to tooth enamel, and are compatible with living tissue.

5.10.3.4 Integral Polyelectrolytes

Polyelectrolytes having bound ions integrated in the polymer backbone are called *ionenes*. Some ionenes have been studied for their bacteriostatic and bactericidal activity. Ionenes with segments of polypropylene oxide in the backbone have been evaluated as thermoplastic elastomers.

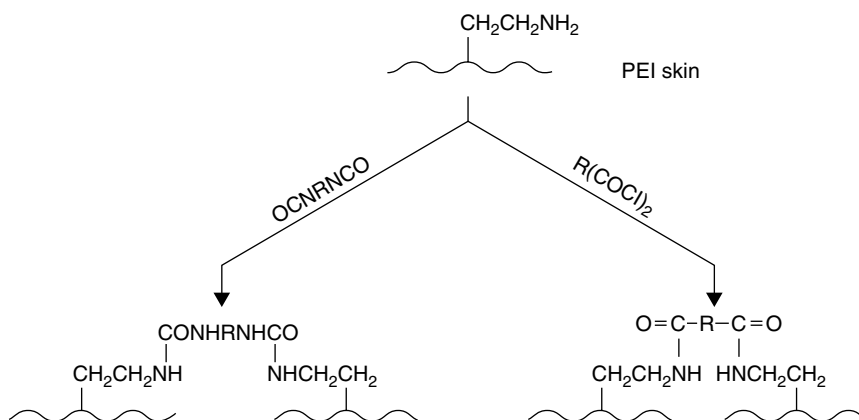
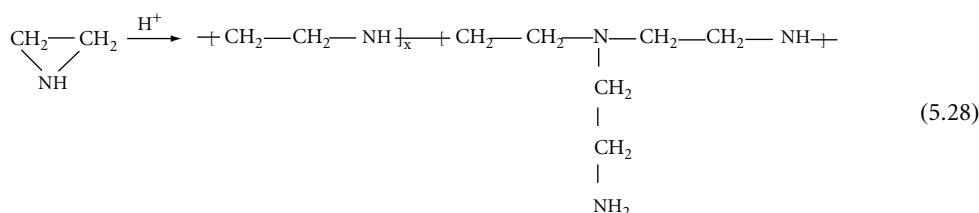


FIGURE 5.65 Insolubilization of polyethylenimine by treatment with toluene diisocyanate or phthaloyl dichloride.

Polyethylenimine (PEI) is an integral polyelectrolyte that is available commercially, e.g., Polymin (BASF). It is formed by the ring-opening polymerization [reaction (28)] of ethyleneimine (aziridine). The resulting polyamine has about 50% of the expected secondary-amine functionality and about 50% primary and tertiary due to branching:



PEI has typical polyelectrolyte properties; it is a highly viscous hygroscopic liquid, completely miscible with water and lower alcohols, insoluble in benzene, and reactive toward cellulose. PEI is mainly used as a size, flocculating agent, or protective colloid, notably in the paper and textile industries, because of its ability to bind to cellulosic fibers.

Membranes based on PEI were introduced for use in reverse osmosis to desalinate water. These membranes, known as NS100 and NS101, are made by forming a PEI skin on polysulfone support and insolubilizing it by treatment with toluene di-isocyanate or phthaloyl dichloride to produce a polyurea or polyamide (Figure 5.65).

5.11 Scavenger Resins

The field of organic chemistry has seen the most extensive use of polymeric materials as aids in effecting chemical transformation and product isolation. Insoluble polymer supports have been used as handles to facilitate these functions. As chemical reagents can be bound to an insoluble polymer carrier and used in organic synthesis [117,118], polymer-bound reagents can also be used to assist in the purification step of solution-phase reactions [119,120]. The latter are known as scavenger resins. These are added to the reaction mixture upon completion of the reaction in order to quench and selectively bind to the unreacted reagents or by-products. The polymer-bound impurities are then removed from the product by simple filtration to obtain pure compounds. For example, aminomethylated poly(styrene-*co*-divinyl benzene) can be used to remove acid chlorides, sulfonyl chlorides, isocyanates, thiocyanates, and proton. Similarly, 2-Chlorotrityl resins have been developed for the attachment of carboxylic acids, alcohols,

phenols, and amines under mild conditions. Several such commercially available examples of scavenger resins are listed in [Table 5.19](#).

5.12 Synthetic Polymer Membranes

A membrane can be described as a thin barrier that permits selective mass transport. This property is described as permselectivity in order to distinguish the membrane from thin nonpermeable film or layer. The mode of permeation and separation is dictated by its morphology. The basic morphologies are isotropic (dense or porous) and anisotropic with a tight surface extending from a highly porous wall structure [121]. While the transport rate through a dense membrane is inversely proportional to the membrane thickness, membrane permselectivity is independent of thickness. Thus anisotropic membranes permit both high transport rates and excellent separation, eliminating the mechanical integrity problems associated with the handling of ultrathin membranes. This concept has led further to the development of thin-film composite membranes which consist of ultrathin semipermeable layers on highly porous substrates as support offering minimum resistance to the permeates. In this way, materials that exhibit semipermeable properties but cannot form self-supporting membranes can be deposited on other porous substrates. For example, a polysulfone porous-support matrix is coated with cross-linked polyethyleneimine (PEI)-toluene diisocyanate (TDI) or furan resin as dense layers of 0.1–1 μm thickness to produce composite membranes. The permeability of such membranes depends on the porosity of the substrates and the complex composition of the deposited permselective layer [121].

As permselective barriers, synthetic membranes have been employed in a variety of applications, which include dialysis, microfiltration, ultrafiltration, reverse osmosis, pervaporation, electrodialysis, and gas separation. Synthetic membranes also find special applications as permselective barriers for ion-specific electrodes, biosensors, controlled release, and tissue-culture growth. Some commercial polymer membranes are listed in [Table 5.20](#).

5.12.1 Membrane Preparation

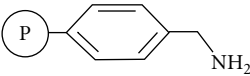
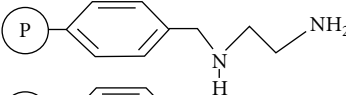
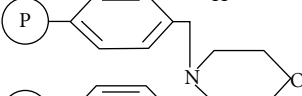
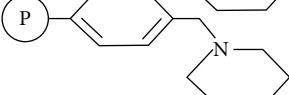
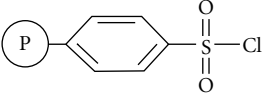
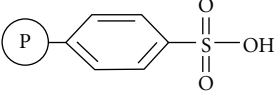
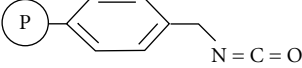
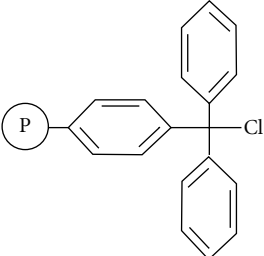
Most of the membranes listed in [Table 5.20](#) are formed through phase separation processes, i.e., melt extrusion or coagulation of a polymer solution by a nonsolvent. In melt extrusion, a polymer melt is extruded into a cooler atmosphere which induces phase transition. The melt extrusion of a single polymer usually gives a dense, isotropic membrane. However, the presence of a compound (latent solvent) that is miscible with the polymer at the extrusion temperature but not at the ambient temperature, may lead to a secondary phase separation upon cooling. Removal of the solvent then yields a porous isotropic membrane. Anisotropic membranes may result from melt extrusion of a dope mixture of polymers containing plasticizers.

Membranes are prepared from polymer(s) dissolved in a solvent using either a dry process or a wet process. In the dry process, a volatile solvent is used for dissolving the polymer(s) and the extruded polymer solution is transferred into an evaporation chamber to yield a porous, isotropic or anisotropic membrane. In the wet process, on the other hand, the extruded mixture is coagulated by exposing the mixture to a nonsolvent in the form of vapor or liquid. The latter process is often referred to as the phase inversion process.

5.12.1.1 Wet-Extrusion Process

Membranes used in microfiltration, reverse osmosis, dialysis, and gas separation are usually prepared by the wet-extrusion process, since it can be used to produce almost every membrane morphology. In the process, homogeneous solutions of the polymers are made in solvent and nonsolvent mixtures, while phase inversion is achieved by any of the several processes, such as solvent evaporation, exposure to excess nonsolvent, and thermal gelation. In most formulations, polymer solutions of 15–40 wt% concentration are cast or spun and subsequently coagulated in a bath containing a nonsolvent (usually water).

TABLE 5.19 Some Commercially Available Scavenger Resins

Resin Name	Structure	Reacts With
Poly(Styrene- <i>co</i> -divinyl benzene), aminomethylated		RCOCl, RSO ₂ Cl, RNCO, RNCS, H ⁺
Ethylenediamine polymer-bound		RCOCl, RSO ₂ Cl, RNCO, RNCS, H ⁺
Morpholine, polymer-bound		H ⁺
Piperidine, polymer-bound		H ⁺
Sulfonyl chloride polymer-bound		ROH, RNH ₂
P-Toluenesulfonic acid, polymer-bound		ROH, RNH ₂
Isocyanate, polymer-bound		RNH ₂ , RNHNH ₂ , RO [•]
2-Chlorotrityl chloride, polymer-bound		RCO ₂ H, ROH, phOH, RNH ₂

Source: Catalog of Sigma-Aldrich Corporation, Milwaukee, WI, U.S.A.

TABLE 5.20 Some Commercial Polymer Membranes and Their Applications

Material	Applications ^a
Cellulose acetate (CA)	MF, UF, RO, D, GS
Cellulose triacetate (CTA)	MF, UF, RO, GS
CA-CTA blend	RO, D, GS
Cellulose esters, mixed	MF, D
Cellulose, regenerated	MF, UF, D
Polyamide, aromatic	MF, UF, RO, D
Polyimide	UF, RO
Polyacrylonitrile	UF, D
Polysulfone	MF, UF, D, GS
Polytetrafluoroethylene	MF
Poly(vinylidene fluoride)	MF, UF
Polypropylene	MF
Polydimethylsiloxane	GS

Source: Cabasso, I., 1987. *Encyclopedia of Polymer Science and Engineering*, Vol. 9, J. I. Kroschwitz, ed., Wiley-Interscience, New York.

^a MF, microfiltration; UF, ultrafiltration; RO, reverse osmosis; D, dialysis; GS, gas separation.

The polymer concentration in the solution is adjusted depending on the viscosity. Higher solution viscosities are required for the production of hollow-fiber membranes, as compared to flat sheet production, because the fiber fabrication is performed without a casting surface.

The morphology of the membrane is strongly influenced by the concentration gradient of the permeating coagulant (nonsolvent) within the cast layer. If the concentration profile is flat, coagulation occurs virtually the same time over the entire layer, yielding an isotropic porous membrane. This happens, for example, when the membrane is precipitated by exposing the cast layer to the coagulant vapor phase or if solvents with low vapor pressure are used. On the contrary, if the concentration gradient of the permeating coagulant is steep, as when membranes are coagulated in a nonsolvent bath, an anisotropic porous membrane forms, which can be used for ultrafiltration, reverse osmosis, and gas separation.

Thermally induced phase separation (TIPS) in polymer solutions is one of the most versatile and widely used methods for the production of microporous membranes [122]. In the TIPS process, a homogeneous solution is formed by the dissolution of a polymer in a diluent at a high temperature and phase separation is then induced by cooling the polymer solution. The compatibility between the polymer and the diluent is one of the key factors affecting the morphology of the membrane. In many cases, polyolefin has been used as the polymer material to prepare microporous membranes [123,124]. A high-density polyethylene hollow-fiber membrane has been prepared by polymer crystallization via the TIPS process [125]. Poly(ethylene-co-vinyl alcohol) hollow fiber membranes with 44 mol% ethylene content, showing better pore connectivity and rejection of ~ 20 nm diameter solute, has been prepared by TIPS, using a mixture of 1,3-propanediol and glycerol (50:50) as diluent [126].

Polymers containing ethylene oxide units are of considerable interest since ether oxygen linkages lead to flexible polymer chains and specific interactions with metal ions, polar molecules such as H₂O and H₂S, and quadrupolar molecules such as CO₂. Thus rubbery membrane materials have been made for the removal of acidic gases such as CO₂ and H₂S from natural gas (mainly CH₄) using a highly branched, cross-linked PEO hydrogel (see below). Unlike conventional size-sieving membrane materials, which achieve high permeability selectivity mainly via high diffusivity selectivity, these polar rubbery membrane materials exhibit high CO₂ permeability and high CO₂/CH₄ mixed-gas selectivity due to high gas diffusivity and high CO₂/CH₄ solubility selectivity [127].

In a typical method of preparation of the aforesaid rubbery membrane material [127], a prepolymer solution is prepared by adding 0.1 wt% initiator (e.g., 1-hydroxy-cyclohexyl phenyl ketone) to poly(ethylene glycol) diacrylate (PEGDA, 743 g/mol) or mixtures of PEGDA and poly(ethylene glycol) methyl ether acrylate (460g/mol). After mixing and sonicating to eliminate bubbles, the solution is

sandwiched between two quartz plates separated by spacers to control thickness and polymerized by exposure to 312 nm UV light for 90 s at 3 mW/cm².

Compared to flat membranes, hollow-fiber membranes have much wider applications at the commercial scale because they provide a higher membrane area per unit membrane module volume.

5.12.1.2 Hollow-Fiber Membranes

Integrally skinned asymmetric membranes used for gas and liquid separations consist of a thin skin layer supported by a porous substructure. The skin layer determines the permeability and selectivity of the membrane, whereas the porous substructure functions primarily as a physical support for the skin. Both layers are composed of the same material and are integrally bonded. The skin layer usually has a thickness on the order of several hundred to several thousand angstroms.

At present, hollow-fiber membranes used for gas and liquid separations are mostly prepared from amorphous polymers by means of a phase inversion technique. In this technique, a polymer is dissolved in a suitable solvent or solvent mixtures and spun into a coagulation bath, where solvent exchange occurs between the extruded fiber and coagulant, yielding the asymmetric membrane structure.

Technology development on the fabrication of asymmetric membranes with an ultrathin dense layer has received much attention due to the fact that the thinner the dense layer is, the higher is the productivity. The fabrication of a hollow fiber with a desirable pore-size distribution and performance is not a trivial process as many factors influence fiber morphology during the phase inversion.

The controlling factors for hollow fiber spinning are not only complicated, but also quite different from those for flat membranes. For example, two coagulations take place in hollow fiber spinning (at internal and external surfaces), while there is only one major coagulation surface for an asymmetric flat-sheet membrane. Moreover, whereas there is usually a waiting period for an asymmetric flat membrane before immersing it into a coagulant, the internal coagulation process for a hollow fiber, if liquids are used as *bore* fluids, starts immediately after extrusion from a spinneret and the fiber then goes through the external coagulation. In addition, the spinning dope suitable for fabricating hollow fibers generally has a much greater viscosity and elasticity than that for flat membranes. Furthermore, the phase

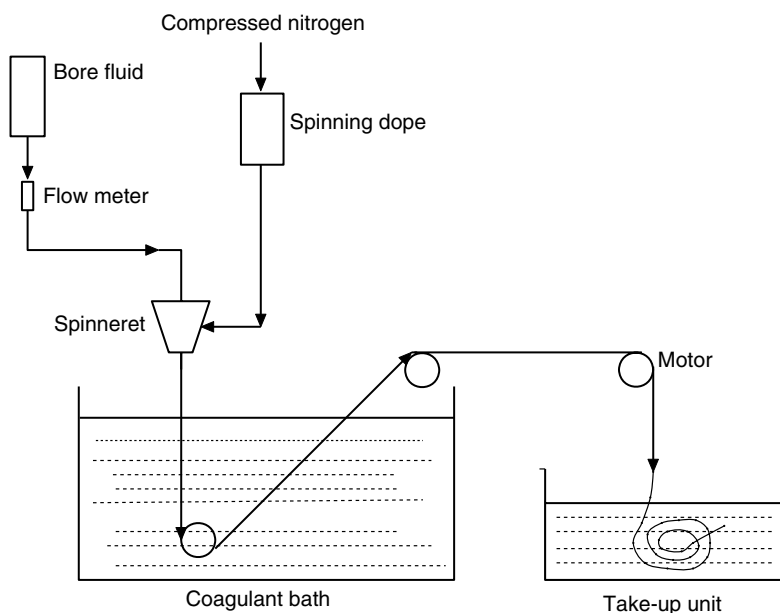


FIGURE 5.66 Schematic diagram of a hollow-fiber spinning process. (After Chung, T. S. and Hu, X. 1997. *J. Appl. Polym. Sci.*, 66, 1067. With permission.)

inversion process for hollow-fiber formation usually takes place under tension or elongational stress, while flat membranes do not experience this type of stress [128].

A typical hollow-fiber spinning set-up is shown in Figure 5.66. For poly(ether sulfone) (PES) hollow fiber [128] a spinning solution (dope) of PES (30%) in *N*-methyl-2-pyrrolidone (NMP) is extruded under a nitrogen pressure of 10 psi through a spinneret having dimensions (typically) of 800 and 550 μm for outer and inner diameters, respectively. The bore fluid of composition NMP/water (40/60) is conveyed by the gravity force through a flow meter. The spinning dope and the bore fluid, flowing at the rate of 0.317 and 0.083 cm^3/min , respectively, meet at the tip of the spinneret, then pass through an air gap ranging from 0 to 14.4 cm before entering the coagulation (water) bath. Once a hollow fiber is formed, it is stored in water bath for several days and then transformed to a tank containing methanol to remove the residual NMP completely.

The air gap distance between the spinneret and coagulation bath (see Figure 5.66) plays a very important role on fiber performance. An increase in air-gap distance may result in a significant decrease in permeance. This may arise from the fact that different precipitation paths arise during the wet-spinning and dry-jet wet-spinning processes. As illustrated in Figure 5.67, the nascent hollow fiber experiences vigorous and rapid coagulation at its internal and external surfaces simultaneously in a wet-spinning process. However, in a dry-jet wet-spinning process the nascent as-spun fiber experiences two different coagulation paths (see Figure 5.67) before entering the coagulation bath, viz., a vigorous coagulation at its internal surface and a nonvigorous coagulation at its external surface. A big air-gap distance may thus produce a greater orientation and tighter molecular packing at the outer surface, causing a decrease in permeance. The difference between the coagulations of the two spinning processes is further explained below.

Since in a wet-spinning process (Figure 5.68), the as-spun fiber is immersed in the non-solvent coagulation bath immediately after exiting from the spinneret, the coagulations at both inner and external surfaces are vigorous and rapid with the result that the extended and randomly oriented polymer chains contract suddenly and almost instantaneously, thereby entrapping a significant amount of non-solvent and solvent in the contracted chains [128]. Both the outer and inner skin layers formed may, therefore, have a long-range random and entangled structure with some macro/microporosity or free volume.

In the case of dry-jet wet-spinning process (Figure 5.68) with a certain air-gap distance, the moisture-induced precipitation process slows the speed of chain contraction and provides contracting chains with time needed for conformation rearrangement [128]. The external surface layer of a hollow fiber made by this process may thus have compact short-range random arrangement of polymer chains in circumferential and lateral directions, and a slightly oriented and stretched structure in the axial direction, producing a skin morphology that has less micro- and macroporosity or free volume. The dry-jet wet-spun fibers thus have more compact structure than wet-spun fibers.

5.12.2 Membrane Modules

Mainly four types of membrane modules are used: plate-and-frame, spiral-wound, tube-in-shell, and hollow fiber. The plate-and-frame module consists of a series of membranes (10–500 μm thick) sandwiched between spacers that act as flow channels (Figure 5.69). (The membranes are often laminated on a porous support that offers no flow resistance.) The feed flows in one set of channels and the permeate, with or without carrier fluid, flows in alternate channels. Plate-and-frame modules find use in ultrafiltration and dialysis applications which include hemodialysis and electrodialysis.

In the spiral-wound system, membranes glued together at the ends and separated by spacers (that provide flow channels to the feed and permeate) are layered and wound around a central porous tube several times, thus forming a multilayered and cylindrical module. The feed mixture flows axially into the channels and the permeate flows spirally into a central porous tube and out of the system. A spiral-wound module has at least twice the packing density of a plate-and-frame module. Several spiral-wound modules can be lined up in series forming a cartridge system.

The tube-in-shell modules usually consist of porous tubes with the membrane attached either inside or outside depending on the application and are especially suited to handle liquids that contain suspended

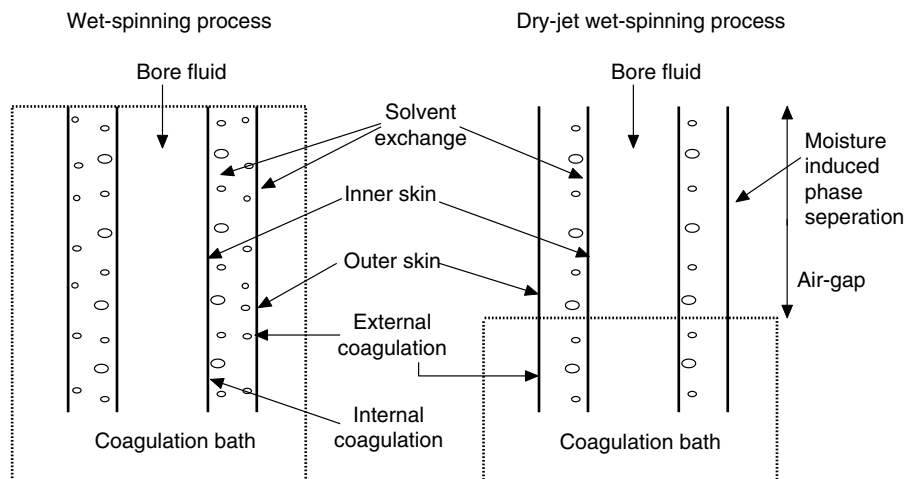


FIGURE 5.67 Comparison of precipitation in the wet-spinning and dry-jet wet-spinning processes. (After Chung, T. S. and Hu, X. 1997. *J. Appl. Polym. Sci.*, 66, 1067. With permission.)

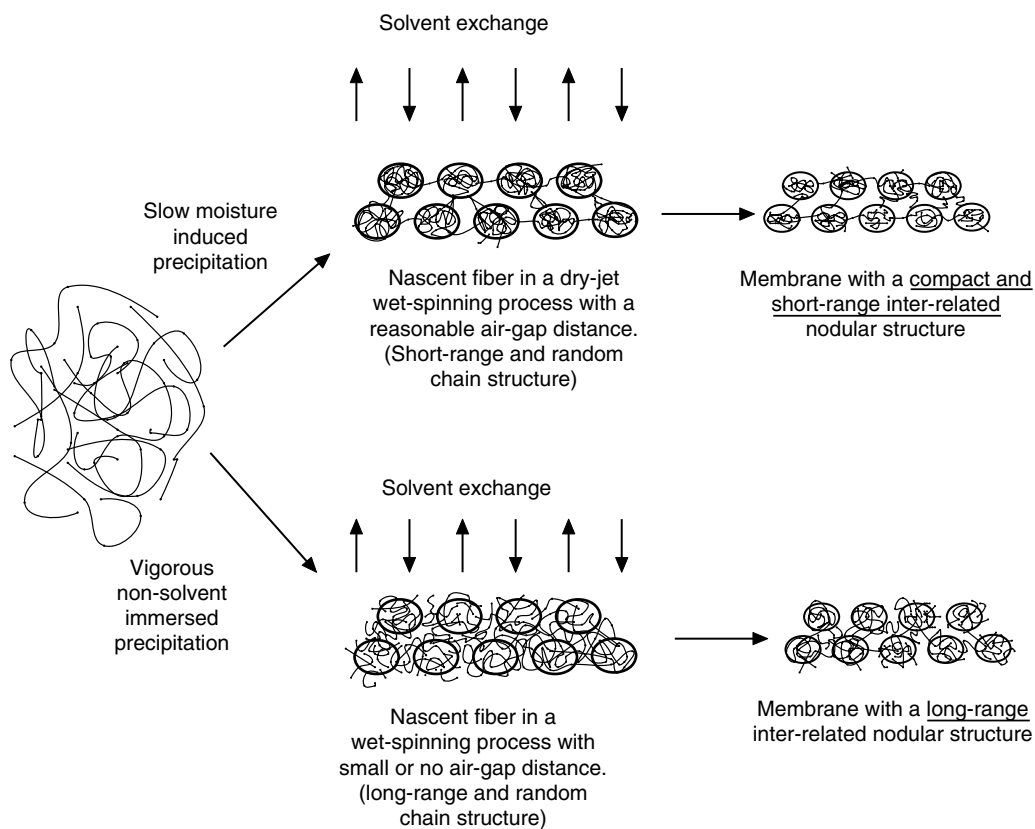


FIGURE 5.68 Schematic of skin morphologies in the wet-spinning and dry-jet wet-spinning processes. (After Chung, T. S. and Hu, X. 1997. *J. Appl. Polym. Sci.*, 66, 1067. With permission.)

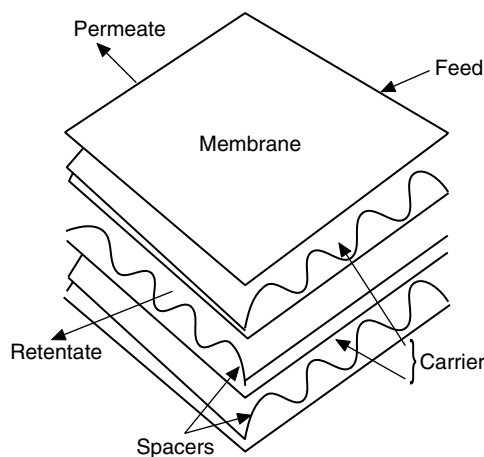


FIGURE 5.69 Schematic of a plate-and-frame type multilayer membrane module.

solids and colloids. When the feed liquid contains a high concentration of suspended solids, membranes with higher tube diameters are often used sacrificing packing density. Tube-in-shell modules are suited for high flux operations in ultrafiltration and reverse osmosis where deposits resulting from concentration polarization tend to clog other configurations rapidly. In these modules, the deposits on single tubes can be easily removed and tube replacement is inexpensive.

Hollow fibers have two advantages over flat sheet or tubular membranes, viz., they provide higher productivity per unit volume and they are self-supporting. The higher productivity results from the fact that surface-to-volume ratio varies inversely with fiber diameter. Thus with hollow fibers of 100 μm diameter, a 0.3 m^3 device can offer 500 m^2 of effective membrane area, as compared to about 20 m^2 for flat-sheet membrane and about 5 m^2 for

membrane in tubular form. As hollow fibers are self-supporting, the hardware requirement for the fabrication of a hollow-fiber unit is simple. Unlike flat-sheet membranes which must be assembled (see Figure 5.69) with spacers, porous supports, etc., a hollow fiber module can be made by simply potting a bundle of hollow fibers into a plastic or metal tube (Figure 5.70). The hollow-fiber unit is, however, vulnerable to fouling and clogging by suspended particulates in the feed. Thorough pretreatment of the feed is therefore necessary.

The most important applications of hollow-fiber modules are in hemodialysis (Figure 5.70), reverse osmosis, and gas separation units. Modules up to 50 cm diameter containing hundreds of thousands of fibers are used in gas separation.

5.12.3 Applications

In hemodialysis, low molecular metabolic waste such as urea, creatinine, and other toxic substances (solutes up to 6000 mol wt) are removed from the blood of uremia patients by diffusive transport, which is driven by a concentration gradient of blood solutes being dialyzed against a physiological solution. A complimentary process is hemofiltration, in which solutes up to 20,000 mol wt are removed via an ultrafiltration membrane, the transport being caused by a convective transmembrane flux generated by mild hydraulic pressure differences across the membrane.

Several classes of polymeric materials are found to perform adequately for blood processing, including cellulose and cellulose esters, polyamides, polysulfone, and some acrylic and polycarbonate copolymers. However, commercial cellulose, used for the first membranes in the late 1940 s, remains the principal material in which hemodialysis membranes are made. Membranes are obtained by casting or spinning a dope mixture of cellulose dissolved in cuprammonium solution or by deacetylating cellulose acetate hollow fibers [121]. However, polycarbonate-polyether (PC-PE) block copolymers, in which the ratio between hydrophobic PC and hydrophilic PE blocks can be varied to modulate the mechanical properties as well as the diffusivity and permeability of the membrane, compete with cellulose in the hemodialysis market.

Low-density polyethylene and polypropylene in the form of flat-sheet and hollow-fiber membranes are used in plasmapheresis and as oxygenators in the heart-lung machine. Other materials commonly used in plasmapheresis are cellulose acetate, polycarbonate, and polysulfone [129].

Membrane technology is employed in the separation of gases, e.g., H_2 from N_2 , CO , and CH_4 ; CO_2 and water vapor from natural gas. It finds use in H_2 recovery from ammonia production plants. The

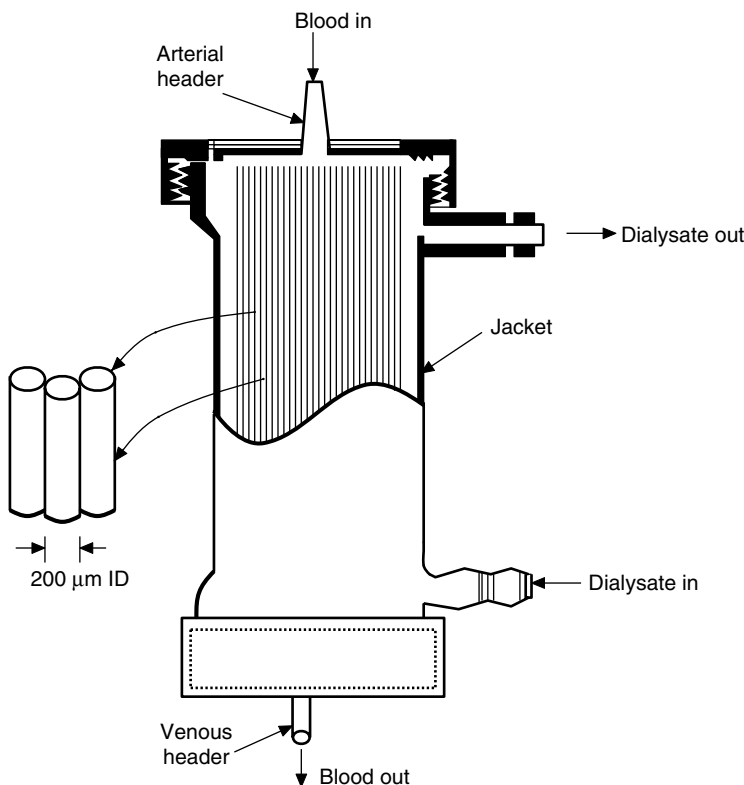


FIGURE 5.70 Schematic of a hollow-fiber membrane cartridge used for blood dialysis.

separation of gas components by polymer membranes is based on chemical affinities and kinetic (sieving) diameters of gases, e.g., He 0.26, H₂ 0.289, CO₂ 0.33, O₂ 0.346, N₂ 0.364, CH₄ 0.38 nm [130]. At low pressures, the membrane selectivity is closely related to the separation factor, $\alpha_{AB} = (S_A/S_B) (D_A/D_B)$, where S_A/S_B represents the preferential sorption or solubility and D_A/D_B is the ratio of diffusion coefficients (mobilities) of the components A and B. In general, high diffusions and solubilities are associated with the rubbery polymer as it has high mobility of chain segments and higher rate of increase of free volume with temperature, as compared to the glassy polymer.

Oily water wastes constitute a major environmental problem in many industries. Stable oil/water emulsions, which cannot be broken by mechanical or chemical means, require more sophisticated treatment to meet the effluent standards. Various physical methods including microfiltration, ultrafiltration, nanofiltration, centrifugation, air flotation, and fiber or packed bed coalescence have been applied in oil-surfactant-water separation [131]. Among these physical methods, membrane technology is by far the most widely used.

In an effort to improve resistance to fouling, hydrophilic and low surface charge membranes have been developed because hydrophilic materials are less sensitive to adsorption than hydrophobic ones. Using polyetherimide as the membrane material and polybenzimidazole and poly(ethylene glycol) as the additives, hydrophilic hollow-fiber membranes have been prepared for oil-surfactant-water separation [132], showing rejection rates of 51%–79%, 83%–93%, and more than 99% for surfactant, total organic carbon, and oil, respectively. Polyetherimide hollow-fiber membranes have also been prepared using polyvinylpyrrolidones as additives for separation of oil-surfactant-water emulsion systems [133], achieving the corresponding rejection rates of 76%–80%, 91%–93%, and more than 99%. Figure 5.71 shows the flow diagram of a typical oil-surfactant-water membrane separation system.

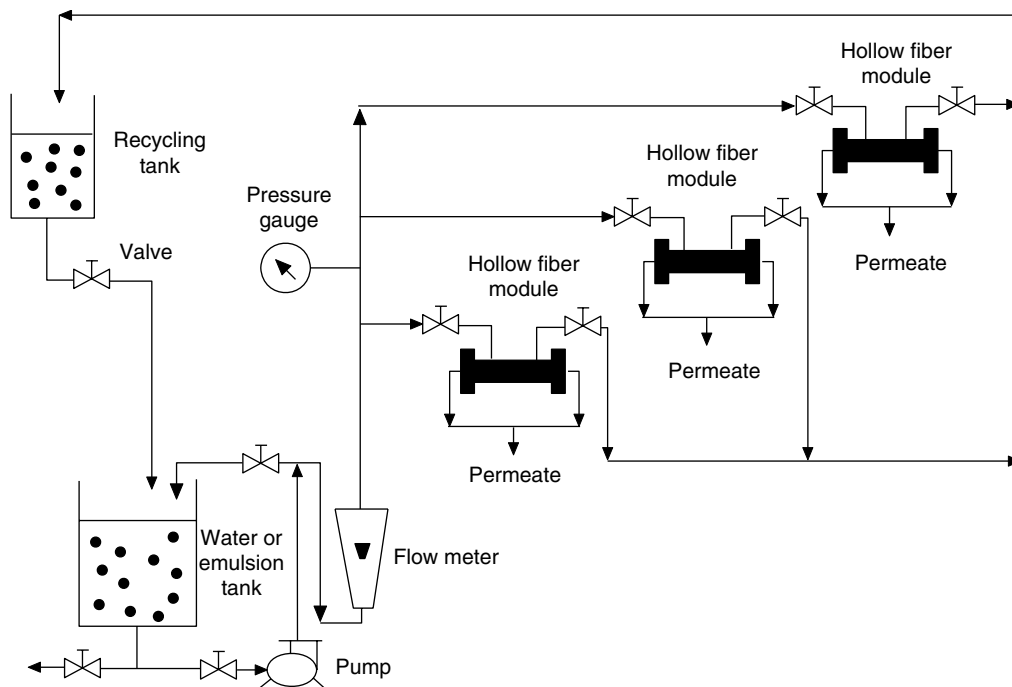


FIGURE 5.71 Flow chart of a separation unit using hollow fiber membranes for oil-surfactant-water emulsion systems. (After Xu, Z. L., Chung, T. S., Loh, K. C., and Lim, B. C. 1999. *J. Appl. Polym. Sci.*, 158, 41. With permission.)

5.13 Hydrogels and Smart Polymers

Hydrogels are three-dimensional hydrophilic polymer networks that absorb water but do not dissolve in water. The extent of volume change due to water absorption varies with the degree of ionization of the gel and for a superabsorbent it may be as large as 500 fold. The volume change is understood as a phase transition which is a manifestation of competition among three forces on the gel—the positive osmotic pressure of counterions, the negative pressure due to polymer-polymer affinity, and the rubber elasticity of the polymer network [134]. The balance of these forces varies with changes in temperature or solvent properties.

Partially hydrolyzed and lightly cross-linked polyacrylamide is a typical superabsorbent hydrogel. The polyacrylamide gels are prepared by free-radical polymerization. In a typical procedure [134], acrylamide (linear constituent), *N,N'*-methylene-bisacrylamide (tetrafunctional cross-linking constituent), and *N,N,N',N'*-tetramethyl ethylene diamine (TEMED) (accelerator) are dissolved in (degassed) water at 0°C to which ammonium persulfate (initiator) is added to initiate polymerization. The polymerization is typically done in micropipettes, although gels have also been alternatively synthesized between glass plates with spacers. (In many other systems, other comonomers, preferably with ionic groups, are added to achieve desired properties.) After gelation, the cylindrical samples from capillaries or sliced pieces from a macroscopic product are dialyzed with water to remove residual monomers and then partially hydrolyzed to convert a part of the amide groups to carboxylic acid groups:



The possibility of using superabsorbent hydrogels as water managing materials for the renewal of arid and desert environments has attracted great attention [135]. These materials can reduce irrigation

water consumption, improve fertilizer retention in soil, lower the plant death rate, and increase the plant growth rate [136]. However, the application of superabsorbents in this field has been limited because most polymeric superabsorbents are based on pure poly(sodium acrylate) and so they are too expensive and not suitable for saline water and soils [137]. In order to reduce production costs and improve salt resistance, superabsorbent composites have been made by incorporating mineral powders into hydrogels [138,139].

Fertilizers are as important as water in agriculture and horticulture. However, about 40%–70% fertilizer is lost to the environment and cannot be absorbed by crops and trees when mixed with soil directly, resulting in large resource losses and serious environmental pollution [140]. Incorporating fertilizers into a superabsorbent polymeric network may thus be an effective way of increasing the utilization efficiency of both water and fertilizer [141]. Thus a multifunctional superabsorbent composite based on poly(acrylic acid-co-acrylamide) (PAA-co-AAm) has been obtained by incorporating sodium humate (SH), which can perform a number of functions such as regulate plant growth, accelerate root development, improve soil cluster structures, and enhance the absorption of nutrient elements. In a typical procedure, 3.6 g of AAm, 4.3 g of AA (50% neutralized with 2M sodium hydroxide solution) and 8.8 mg *N,N'*-methylenebisacrylamide (cross-linking agent) are polymerized with ammonium persulfate as initiator for 3 h at 50°C, in the presence of an appropriate amount of SH dispersed in the mixed solution. The product is washed with water and ethanol and then dried in an oven at 70°C.

The superabsorbent composites containing SH show release of the fertilizer over 10–40 days, depending on the SH content (5 wt% to 30 wt%). The release rates into water in the initial period are higher since the SH existing on the surface or freely incorporated in the composite network are dissolved more readily in water. The SH bonded with the polymeric network needs more time to diffuse from the hydrogel granule and dissolve in water. Figure 5.72 shows schematic structures of a PAA-co-AAm/SH

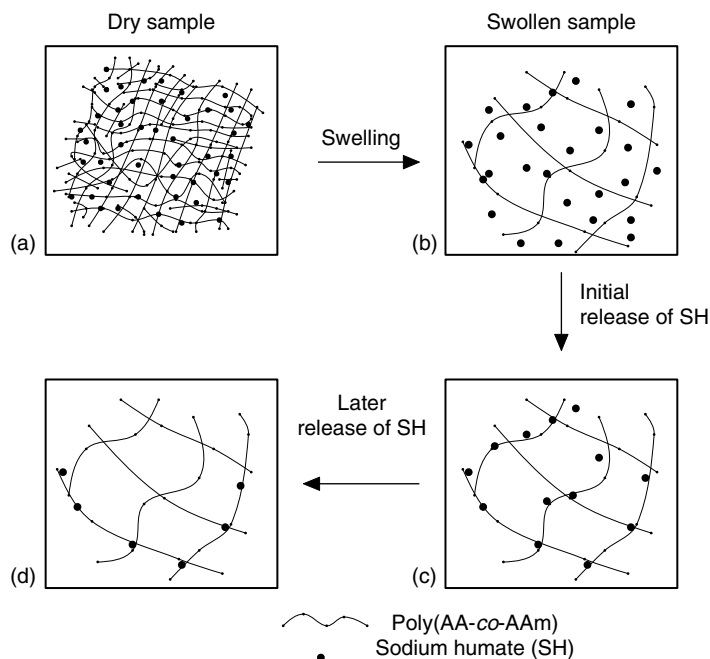
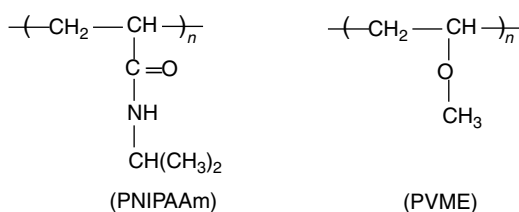


FIGURE 5.72 Schematic structures of a PAA-AM/SH superabsorbent composite (see text): (a) in dry state; (b) in swollen state; (c) after release of SH which is on the surface or freely incorporated in the polymer network; and (d) after release of SH that is bonded with the polymer network. (After Zhang, J., Liu, R., Li, A., and Wang, A. 2006. *Ind. Eng. Chem. Res.*, 45, 48. With permission.)

superabsorbent composite in the dry state, in the swollen state, and after the release of SH. The superabsorbent composite also improves the water-retention capacity of the soil. Thus, compared to sand soil without the superabsorbent composite, 33.45 wt% water was still retained on the 20th day when the sand soil was mixed with 1.0 wt% composite containing 30 wt% SH [141].

5.13.1 Smart Polymers

Stimuli-responsive hydrogels which exhibit volume changes or phase transitions in response to differences and variations in the surrounding environment, such as temperature [142], pH [143], pressure [144], electricity [145], or light [146] are given the term smart or intelligent because their strange properties can be put to use in a wide range of applications. Two of the most studied polymers in the intelligent materials stage are poly(*N*-isopropylacrylamide) or PNIPAAm and poly(vinyl methylether) or PVME.



Both PNIPAAm and PVME exhibit unique thermo-shrinking properties. Thus, as an aqueous solution is heated beyond a certain point, the polymer shrinks and a phase separation occurs. This temperature is commonly referred to as the lower critical solution temperature (LCST). For PNIPAAm, it lies between ca. 30 and 35°C, the exact temperature being a function of the detailed microstructure of the macromolecule. Below LCST, the polymer is soluble in the aqueous phase, as the chains are extended and surrounded by water molecules. Above the LCST, the polymer becomes insoluble and phase separation occurs. Because of the abrupt nature of these transitions and their reversibility (which allows repeated thermal switching) these polymers have stirred up particular interest in the field of science and engineering since their first appearance in the open literature in 1956.

PNIPAAm has been synthesized from *N*-isopropylacrylamide (NIPAAm) by a variety of techniques, the most widely used being free-radical initiation of organic solutions [147] and redox initiation in aqueous media [148]. Redox polymerization of NIPAAm in aqueous media typically uses ammonium persulfate or potassium persulfate as the initiator and either sodium metabisulfite or *N,N,N',N'*-tetramethylethylenediamine (TEMED) as the accelerator. In addition, the solutions are usually buffered to constant pH since in the absence of buffer much greater polydispersity is obtained. Whether one polymerizes NIPAAm in organic or aqueous solution also affects polymer properties [149].

One of the very useful applications involving thermo-shrinking polymers is a polymeric tool (a gel hand) made of three layers of PNIPAAm, PAAm, and an inert spacer (Figure 5.73). This gel hand can be used like a tweezer to pick up a target compound in aqueous solution by simply raising the temperature above LCST and to release the compound below LCST.

Thermoresponsive polymers can also be used in many biotechnological applications. The use of such polymers for in vitro studies allows the control of surface properties and thus the stimulation of cell adhesion and detachment through temperature changes. For example, normally an enzyme would be used to detach cultured tissue cells from culture dishes for further culturing, but the process is very inefficient because many of the detached cells are damaged by the enzyme. This problem has been overcome by using PNIPAAm which aids cell adherence by exhibiting hydrophobicity above its LCST, but below this temperature the polymer exhibits hydrophilicity and binds to water thus pushing the cells away. Therefore, by lowering the temperature just below the LCST of the polymer, almost all of the cells can be detached for culturing. This process is simple, efficient, inexpensive and polymer-grafted dishes can be re-used many times.

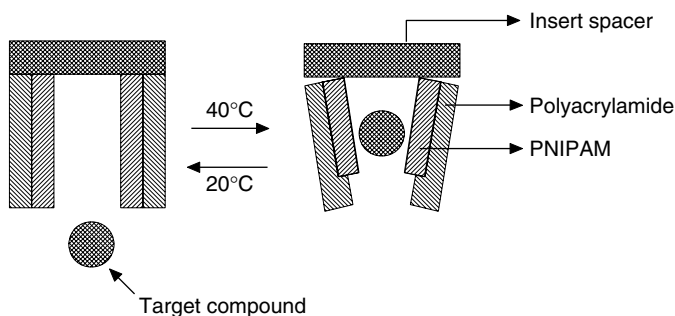


FIGURE 5.73 A schematic illustration showing how thermo-shrinking polymer PNIPAAm can be used as a gel hand to isolate a target compound.

In an interesting biochemical application, PNIPAAm has been attached near the receptor site of the protein Streptavidin, which binds to the ligand biotin with a very large association constant. Below LCST ($\sim 32^{\circ}\text{C}$) of PNIPAAm, the polymer is a soluble random coil and allows the binding of the ligand to the protein. However, above the LCST, the polymer molecule collapses onto the receptor site, preventing the binding of the ligand to the protein. This reaction can thus be controlled by small changes in the temperature. Since protein-ligand interactions are used in many assay procedures, such as immunoassays, the above ability to control ligand binding can find many applications in biotechnology and medicine.

In recent years, many kinds of temperature-responsive PNIPAAm and its copolymer hydrogels with other acrylic monomers have been synthesized [142]. Besides being used for hydrogels, NIPAAm monomer can be grafted on to polymer substrates by electron beam, irradiation or UV-initiated graft polymerization to achieve special modification of polymer surfaces. Thus NIPAAm has been grafted on porous polymer films such as LDPE, PP, or polyamide films in order to prepare novel films for pervaporation of liquid mixtures or separation membranes [150,151].

LCSTs have been reported [152] for a series of poly(*N*-alkyl acrylamides) which proceed from complete solubility to insolubility as the size of the alkyl side group increases. NIPAAm has also been copolymerized with other *N*-alkyl acrylamides [152,153] over the entire composition range. Typically, continuous changes in the LCST either up or down are observed when the comonomer (with the exception of *N*-*n*-butyl acrylamide) has respectively a smaller or larger *N*-alkyl group than *N*-isopropyl. Thus the LCST of PNIPAAm-like polymers can be shifted from <0 to $>100^{\circ}\text{C}$ by varying the copolymer composition. This provides excellent flexibility in tailoring transitions for specific uses. One can switch off solubility at biologically relevant temperatures as well as room temperature. Moreover, the same LCST can be obtained with a small amount of a very hydrophobic comonomer (such as *N*-decyl) or a high fraction of a less hydrophobic comonomer (such as *N*-*t*-butyl). This permits further modulation of interactions with cosolutes in the system.

PNIPAAm gels have been applied to a myriad applications which exploit the change in gel dimensions to modulate the differential diffusion of species in a medium. It has thus been possible to selectively remove [154,155] and deliver [156–158] cosolutes with thermal-switching control. A few of the processes are described below.

A research group of Cussler at the University of Minnesota did considerable applied research on separations with PNIPAAm gels. Figure 5.74 shows a flow chart of their separation process. It is based on the premise that if a gel is placed into an aqueous solution of a mixture of large cosolute A, such as macromolecules, and small cosolute B (or clean water) (Steps 1 and 2), when the gel swells, A will be excluded from entering the gel pores by steric hindrance and B will freely enter the gel pores. On removing the swollen gel (Step 3), the solution left behind (raffinate) is now more concentrated in A. The removed gel, on the other hand, can be placed into a warm solution to obtain B free of A and the gel

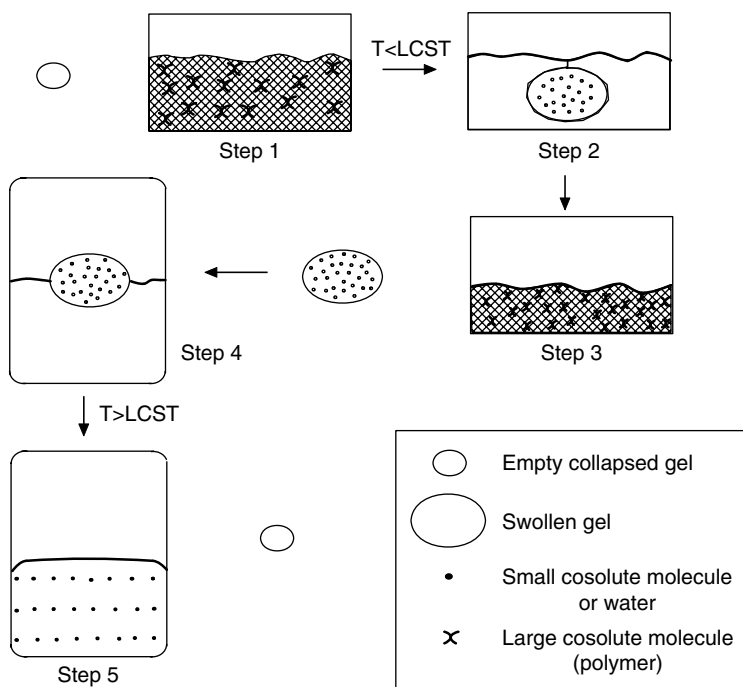


FIGURE 5.74 Steps in separation process using PNIPAAm gel. (After Schild, H. G. 1992. *Prog. Polym. Sci.*, 17, 163. With permission.)

for recycling. The efficiency of the separation process is defined as

$$\text{efficiency} = \frac{\Delta C_R V_R}{V_s^o}$$

where ΔC_R is the measured increase in concentration in raffinate relative to feed, V_R is the volume of raffinate and V_s^o is the initial solution volume. Thus, if the concentration doubles when the volume is halved, then the efficiency is 100%. On the other hand, if the original and final concentrations are the same, then the efficiency is 0%. This separation system has been termed [159] as size selective extraction solvent. It serves as an alternative to ultrafiltration techniques [142].

As would be expected, PNIPAAm gels with higher cross-linking densities yield increased efficiency of separation. However, as cross-links are randomly distributed, there is no abrupt cut-off at an exact molecular weight. Nonetheless, PNIPAAm gel particles have commercial potential as they are able to absorb up to 30 times their dry weight in water [154] and such systems have been patented [155] as an inexpensive alternative to ultrafiltration. The gel separation process has been used for removing low molecular weight contaminants from soy protein [160] and water from gasoline or fuel oils [161]. Polymers in the PNIPAAm class have also been cross-linked into fibrous materials for use as a urine absorbent [162].

Prior to PNIPAAm, the Cussler group [159] used pH-sensitive hydrolyzed polyacrylamide (PAAm) anionic gel, which swells at high pH (and thus picks up small cosolute B); to recover the gel for re-use, the swollen gel is removed and placed in water at low pH when it collapses and squeezes out B. High separation efficiencies are found for species greater than 3 nm in diameter such as proteins and synthetic polymers. However, only negatively charged or neutral species can be separated. Cationic species such as lysozyme cannot be separated as they precipitate on the gel. This is a limitation of the PAAm anionic gel.

Japanese workers [163] have made PVME gels typically through cross-linking with gamma ray irradiation. These exhibit LCST behavior and have been applied in wastewater sludge dewatering, much

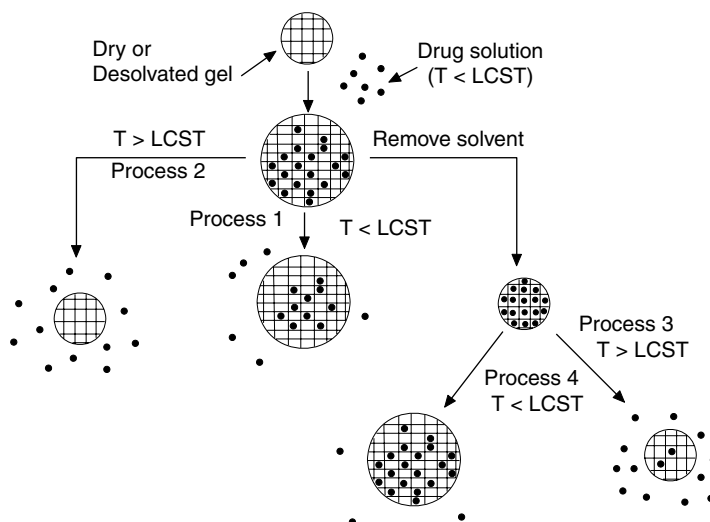


FIGURE 5.75 Various processes of drug delivery using PNIPAAm gel. (After Schild, H. G. 1992. *Prog. Polym. Sci.*, 17, 163. With permission.)

in the same way as PNIPAAm discussed above. The water absorbing rate of the gel varied with the properties and solid concentration of the sludge, as would be expected. Sludges were dewatered by repeated use of the gel.

The application of hydrogels for biomedical applications including drug delivery devices has been of increasing interest. Changes in swelling states of PNIPAAm gels can influence the diffusion of solutes from within the gels to the outside aqueous media [142,156–158,164]. Several different schemes can thus be envisioned for drug delivery application, as shown schematically in Figure 5.75. The LCST of PNIPAAm-type gels can be adjusted to near body temperature (37°C) by copolymerization, by varying the length of the alkyl chain, and by use of additives [142], thus tailoring the drug delivery as desired and making them viable for in vitro applications. Some delivery systems, such as processes 1 and 3 (Figure 5.75), depend on Fickian-type diffusion, while others, such as process 2 (Figure 5.75), may rely on the pressure generated during gel collapse to squeeze out the drug. In process 2, however, after the initial release of drug, there may be increasing retardation in the system due to the formation of a surface skin layer and closure of surface pores as the surface region is the first to contact the solution and undergo the phase transition.

PNIPAAm-based interpreting networks (IPNs) have been developed [158,165]. As the presence of the second polymer (essentially inert) network has little effect on the LCST, it provides the ability to control only the degree of swelling, as was demonstrated [158] by a poly(ethylene oxide–dimethylsiloxane–ethylene oxide)/PNIPAAm system. In contrast, the copolymerization method influences both the degree of swelling and the LCST.

For numerous applications, it is desirable to maximize the volume change with a minute pH change near the phase transition point. A promising candidate [143] for such a system is segmented poly(amine urea) with alternating polar (*N,N'*-diethylenediamine) and apolar (diethylenephénylene) units in the main chain. In a typical method of preparation, an end-isocyanated polyamine was prepared by the 2:1 addition reaction of 4,4'-methylenediphenyldiisocyanate (MDI) to telechelic polyamine having secondary amino groups at both ends and the isocyanated polyamine was then extended by the reaction with equimolar ethylenediamine to form a segmented poly(amine urea) (SPA). The SPA exhibited reproducible swelling/deswelling in response to pH changes, with a discontinuous 270-fold change in the swelling degree at a critical pH indicating a phase transition. The regulation of solute transport across

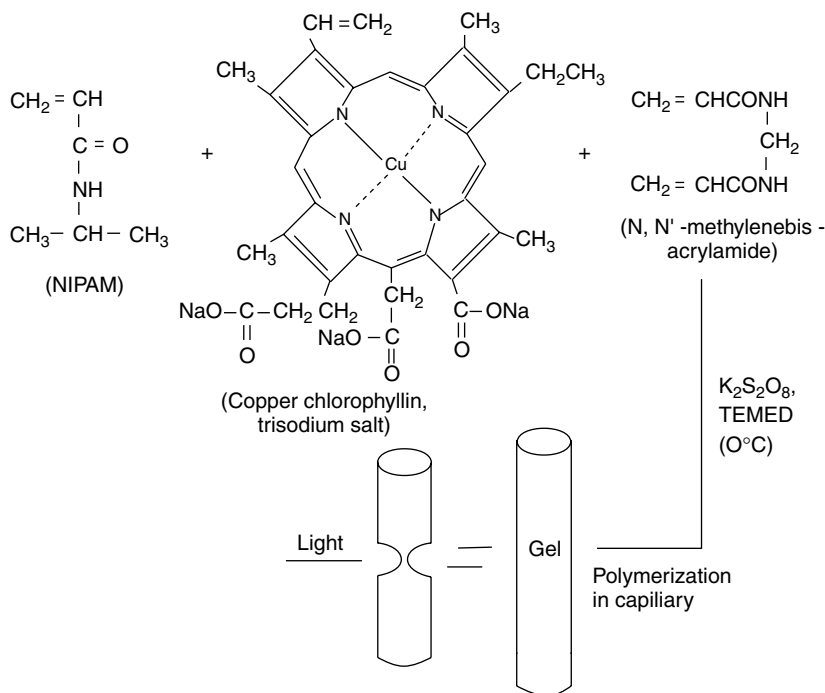


FIGURE 5.76 Preparation of PNIPAAm gel containing light-sensitive chromophore, trisodium salt of copper chlorophyllin. Chlorophyllin has a double bond through which it enters the polymer network forming covalent bonds. The formed gel collapses under illumination. (After Suzuki, A. and Tanaka, T. 1990. *Nature*, 346, 345. With permission.)

the SPAU matrix responding to a pH jump in the external milieu was demonstrated using vitamin B₁₂ as a model solute.

Hydrogels sensitive to ultraviolet light [166] as also those sensitive to visible light [146] have been reported. The ultraviolet light initiates an ionization reaction in the gel, creating internal osmotic pressure which induces swelling, while in the absence of this light, the equilibrium tends towards the neutral polymer system and the gel collapses. This transition process is slow, as it depends on the photochemical ionization and subsequent recombination of ions. It is, however, technologically desirable that the transition be induced by faster mechanisms.

In the visible light induced polymeric gel systems [146], the transition mechanism is due only to the direct heating of the network polymers by light which is an extremely fast process. Such systems might be used as photoresponsive artificial muscles, switches, and memory devices. In a typical method of preparation by free-radical copolymerization (Figure 5.76), 7.8 g *N*-isopropylacrylamide (NIPAAm), 0.72 g trisodium salt of copper chlorophyllin (light-sensitive chromophore), 0.67 g *N,N'*-methylene bisacrylamide (cross-linker), and 240 μl of tetramethylethylenediamine (TEMED) (accelerator) were dissolved in 100 ml water at 0°C , to which 0.2 g of ammonium persulfate was added to initiate the polymerization. Capillaries ($\sim 100\ \mu\text{m}$ diameter) were immersed into the solution. After gelation, the cylindrical samples were removed from the capillaries and dialyzed with water to remove unreacted monomers. Light shrank the gel (Figure 5.76) over the entire temperature range, but the largest effect was seen in the transition region at 31.5°C . For $1\ \mu\text{m}$ diameter gels the response time is expected to be about 5 ms.

In partially hydrolyzed (ionic) acrylamide gels, phase transition can also be induced by the application of an electric field [167]. The electric forces on the charged sites of the network produce a stress gradient along the electric field lines in the gel. There exists a critical stress below which the gel is swollen and

above which the gel collapses. The volume change at the transition is either discrete or continuous, depending on the degree of ionization of the gel and on the solvent composition. The discrete volume transition of the gel induced by an electric field can be used to make switches, memories, and mechanochemical transducers. For example, ionic gels controlled by coordinated signals from a microcomputer may be used as an artificial muscle. Furthermore, two- or three-dimensional images may be stored by using the local collapse and swelling of the gel [167].

One of the problems faced in applying PNIPAAm hydrogels is that the response rate to temperature changes is very slow, which restricts their wider applications, such as on-off valves and artificial muscles. According to the Tanaka-Fillmore theory [168], $\tau \approx R^2/D$, where τ , R , and D are the characteristic time for gel shrinkage, the size of the gel, and the cooperative diffusion coefficient, respectively. It can be observed from this equation that the response time of the gel is proportional, and hence the response rate is inversely proportional, to the square of the size of the gel. Consequently, micrometer-sized gel particles exhibit a more rapid response rate. However, in many applications, bulk hydrogels are needed. Many approaches have therefore been proposed to prepare fast-responsive macroscopic PNIPAAm hydrogels, such as producing phase-separated microstructures in gels [169], preparing comb-type PNIPAAm hydrogels [170], incorporation of silica microparticles, followed by treatment to remove silica [171], polymerization/cross-linking of NIPAAm in solid state [172], polymerizing NIPAAm in salt [173] or saccharide [174], and simple freeze-drying treatment of PNIPAAm hydrogels [175].

Some of the above methods have the limitation that they require the use of strong acids or organic solvents in the gel. A novel, simple, and effective strategy to achieve fast-responsive bulky PNIPAAm hydrogels involves incorporation of PNIPAAm nanoparticles into PNIPAAm networks to form composite hydrogels [176]. PNIPAAm nanoparticles (~ 500 nm) synthesized by emulsion polymerization [176] are dispersed in an aqueous solution of NIPAAm and N,N' -methylenebisacrylamide which are polymerized at room temperature using ammonium persulfate and N,N,N',N'' -tetramethylethylenediamine (TEMED) as initiator and accelerator, respectively. When the polymerization is complete, the generated PNIPAAm chains may pass through the PNIPAAm particles, which would be immobilized in the PNIPAAm networks. In comparison with conventional PNIPAAm hydrogels, the PNIPAAm nanoparticle-incorporated PNIPAAm hydrogels thus prepared exhibit much faster response rates as the temperature is raised above the LCST. These improved response properties are a result of the superfast shrinkage of PNIPAAm nanoparticles which generate pores for water molecules to be quickly squeezed out of the bulky PNIPAAm gels (see Figure 5.77) [176].

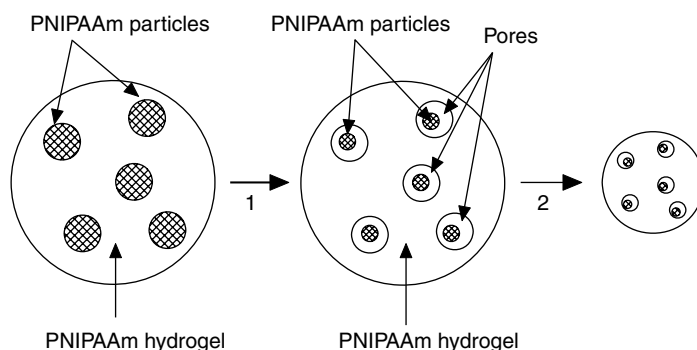


FIGURE 5.77 Schematic illustration of the shrinking process: (1) PNIPAAm particles shrink and generate pores; (2) bulky gels then shrink further at a rapid rate. (After Zhang, J.-T., Huang, S.-W., Xue, Y.-N., and Zhuo, R. X. 2005. *Makromol. Rapid Commun.*, 26, 1346. With permission.)

5.14 Dendritic Polymers

A little more than 30 years after Flory [177] theorized about synthesizing condensation polymers from multifunctional monomers, the first papers on synthesis of dendritic polymers (dendron, Greek for tree) appeared [178,179], revealing a number of very unique and different properties of these polymers, compared to their linear analogs. For instance, at high molecular weights the dendritic polymers were found to be globular and, in contrast to linear polymers, they behaved more like molecular micelles [180]. The descriptors starburst, dendrimers, arborols, cauliflower, cascade, and hyperbranched used for such polymers all describe specific geometric forms of structure.

Following the first papers of Tomalia [178] and Newkome et al. [179] in 1985 dealing with dendrimers, a large number of dendrimers have been presented in the literature ranging from polyamidoamine, aromatic polyethers and polyesters, aliphatic polyethers and polyesters, polypropyleneimine, polyphenylene to polysilane. Copolymers of linear blocks with dendrimer segments (dendrons) and block copolymers of different dendrons have been described.

Dendrimers, as shown in the generalized form in Figure 5.78(a), are obtained when each ray in a star molecule is terminated by an f -functional branching from which $(f-1)$ rays of the same length again emanate. A next generation is created when these $f-1$ rays are again terminated by the branching units from which again rays originate, etc. In recent years, the chemistry of preparing dendrimers has become very successful, although the synthesis of perfect monodisperse dendrimers is time-consuming and painfully cumbersome. Another serious drawback is the space filling due to which it has not been possible to prepare more than five generations. Either the reaction to a higher generation stops completely or, as it happens in practice, the outermost shells develop imperfections.

Though perfect monodisperse dendrimers have very interesting material properties, for use as engineering materials they are far too complicated and costly to produce. This was soon realized by several researchers at DuPont Experimental Station working on dendritic polymers as rheology control agents and as spherical multifunctional initiators. The need to obtain the material rapidly and in large quantities forced them to develop a route for a one-step synthesis of dendritic polymers. These polymers

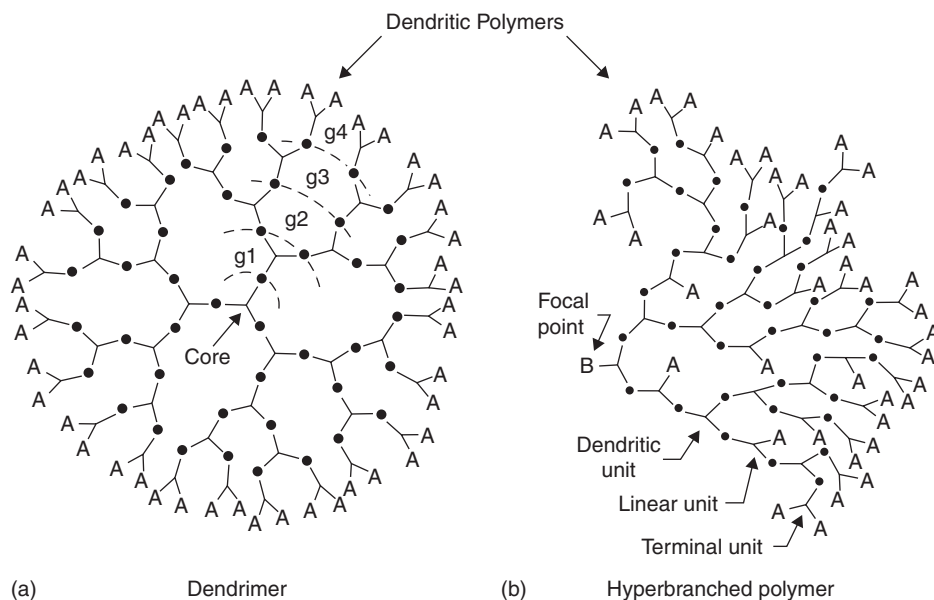


FIGURE 5.78 Schematic representation of dendritic polymers comprising dendrimers and hyperbranched polymers (g level indicates generation number). (After Hult, A., Johansson, M., and Malmström, E. 1999. *Adv. Polym. Sci.*, 143, 1. With permission.)

were, however, polydisperse and had defects in the form of linear segments between branch points but they were highly branched dendritic molecules. Kim and Webster [181] named them hyperbranched polymers. Ever since, a wide variety of hyperbranched polymers have been synthesized and reported in the literature [182].

While in a perfectly branched dendrimer derived from A_xB monomer only one type of repeat unit can be distinguished apart from the terminal units carrying the chain ends [see Figure 5.78(a)], a hyperbranched polymer of A_xB (at high conversion of B) will have three different types of repeat units as illustrated in Figure 5.78(b); these are dendritic units (fully incorporated A_xB monomers), terminal units having two A groups unreacted, and linear units having one A group unreacted. The linear segments are generally described as defects. Since the hyperbranched polymers are allowed to contain some linearly incorporated A_xB monomers, the synthesis of such polymers, unlike that of dendrimers, does not require the use of protection/deprotection steps. The most common synthesis route thus follows a one-pot procedure [183] where A_xB monomers are condensed in the presence of a catalyst. Such one-step polycondensations result in highly branched polymers even though they are not as idealized as the generation-wise constructed dendrimers.

Tedious and repetitive synthetic procedures for dendrimers result in expensive polymers and limit their availability. On the other hand, the one-step process, mentioned above, allows production of hyperbranched polymers on a large scale, giving them an advantage over dendrimers in applications requiring large amounts of material, although the properties of hyperbranched polymers are only intermediate between those of dendrimers and linear polymers. Hyperbranched polymers are also unique in that their properties are easily tailored by changing the nature of the end groups. For some areas, such as coating resins and tougheners in epoxy resins, hyperbranched polymers are envisaged to play an important role. Various other applications of these novel materials have been suggested. One reason for the emerging interest in hyperbranched polymers is their different properties compared to conventional linear polymers.

A step change in hyperbranched polymer synthesis occurred when self-condensing vinyl polymerization was introduced by Fréchet et al. [184], extending hyperbranched methodologies to vinyl monomers with end group control and living polymerization features. Hyperbranched polymer synthesis based on vinyl monomers was developed further by several research groups [185]. An inherent limitation with many of these methodologies, however, is the need for designed functional monomers, which are costly to manufacture and would, therefore, render many cases economically nonviable for large-scale production. In a significant development in this context, Sherrington and co-workers [186,187] have recently demonstrated a new facile route for the synthesis of branched polymers based on commercially available vinyl monomers and the addition of chain transfer agents (CTAs). The stoichiometric balance between the cross-linker [multifunctional monomer (MFM)] and the CTA is the most important parameter that determines whether the polymer remains soluble throughout the reaction or gels and forms a cross-linked network. Thus, hyperbranched poly(methyl methacrylate) has been synthesized using a facile one-step batch solution polymerization reaction, which is essentially a linear polymerization doped with appropriate amounts of MFM and CTA [188].

5.14.1 Applications

Among the various applications suggested for hyperbranched polymers are surface modification, additives, tougheners for epoxy-based composites, coatings, and medicines.

It has been demonstrated that hydrophobic, fluorinated, hyperbranched poly(acrylic acid) films can passivate and block electrochemical reactions on metal surfaces thus preventing surface corrosion [189]. Hyperbranched films can be synthesized on self-assembling monolayers on the metal surface via sequential grafting reactions to obtain thick and homogeneous films.

The lack of mechanical strength makes hyperbranched polymers more suitable as additives in thermoplast applications. Hyperbranched polyphenylenes, for example, have been shown to act

successfully as rheology modifiers when processing linear thermoplastics. A small amount added to polystyrene thus results in reduced melt viscosity [190].

The use of epoxidized hyperbranched polyesters as toughening additives in carbon-fiber reinforced epoxy composites has been demonstrated [191]. The use of hyperbranched polymers as the base for various coating resins has been described in the literature. For example, a comparative study [192] between an alkyd resin based on a hyperbranched aliphatic polyester and a conventional (less branched) high-solid alkyd showed that the former had a substantially lower viscosity and much shorter drying time than the conventional resin of comparable molecular weight.

An important application of dendritic polymers being explored in medicine is in advanced drug delivery systems. However, most applications within this field, described in the literature, deal with dendrimers and not with hyperbranched polymers. In a study on the effect of dendrimer size when used inside the human body, it was found [193] that large dendrimers (M_w ca. 87,000) were excreted into the urine within two days, whereas smaller dendrimers (M_w ca. 5,000) accumulated mostly in the liver, kidney and spleen with no urine excretion. Hyperbranched polymers, being mostly polydisperse, are thus unsuitable in vivo applications.

A special feature of dendritic polymers is the possibility to combine an interior structure having one polarity with a shell (end groups) having another polarity, e.g., a hydrophobic inner structure and hydrophilic end groups. Thus hyperbranched polyphenylenes with (anionic) carboxylate end groups have been described [194], where the carboxylate end groups make the polymer water soluble while the hydrophobic interior hosts non-polar guest molecules. In another example [195], hyperbranched aromatic poly(ether ketone)s having acid end groups have been used to solubilize hydrophobic molecules in water. In such a case, a critical micellar concentration (CMC) is not observed and instead there occurs a steady increase in solubility of the hydrophobic compound with polymer concentration. Such dendritic polymers have been described as unimolecular micelles. In a recent review [196], the guest-host possibility is described for various dendritic polymers considered suitable for medical applications such as drug delivery.

Hyperbranched polymers allow a wide range of variation in properties, which depend on several parameters, the most important however being the backbone and end-group structure in combination. The glass transition temperature, for example, can be shifted 100°C simply by changing the polarity of the end groups, while keeping the backbone structure unchanged.

Though most hyperbranched polymers are considered to be amorphous, some examples of crystalline and liquid crystalline hyperbranched polymers have been described in the literature. The possibility of crystallinity has further expanded the application potential of these polymers. In some cases, in application as toughening additives, the polarity of the hyperbranched polymer relative to the thermosetting matrix resin can be adjusted to give a reaction-induced phase separation in composites, resulting in a dramatic increase in toughness but still retaining the overall good mechanical properties (such as high modulus) of the system. This has been demonstrated for hyperbranched aliphatic polyesters added to epoxy/amine thermoset system. Use as toughening additives for composites represents a successful application of hyperbranched polymers.

Self-assembly, which is a supramolecular approach relying on complementary non-covalent interactions, such as electrostatic interactions and hydrogen bonds, is an incredibly powerful concept in modern molecular science. It offers an attractive option by which small, synthetically accessible, relatively inexpensive dendritic systems (dendrons) can be simply assembled into highly branched complex nanoscale assemblies having wide range of novel properties, that depend on the reversibility and specificity of the assembly process as well as on the branching inherent within the dendritic building blocks. It has been shown [197] that such self-assemblies of dendritic building blocks in solution have potential applications in diverse areas, including controlled release, nanoscale electronics, gel-phase and liquid crystalline materials, and biotechnology.

Dendronized polymers, i.e., polymers with dendritic side chains, are currently under intense investigation with respect to various applications, including the synthesis of hierarchically structured

materials, catalysis, applications in the biosciences, such as ion channel mimics and DNA compactization, as well as photoelectronics applications [198].

Though numerous applications have been suggested for hyperbranched polymers, few have reached the stage of full commercial exploitation. Hyperbranched polymers is, however, a young and growing area in the domain of macromolecules. The special properties of these polymers are now receiving greater attention and a number of interesting applications of the hyperbranched polymers are expected to bring them to the market place. The future thus looks bright for these novel materials.

5.15 Shape Memory Polymers

When a polymer is deformed at a temperature above its glass transition temperature (T_g) and quickly cooled to a temperature below T_g , the deformed shape becomes frozen. An ordinary polymer does not restore its original shape when the temperature is again raised above T_g . But a shape memory polymer (SMP) is known to recover the original shape when it is warmed above T_g . Because of this property, SMPs have drawn wide attention from various fields during the past decade. Figure 5.79 illustrates typical shape memory behavior of a commercially available SMP product. As functional polymers they find applications in a broad range of temperature sensing elements.

SMPs basically consist of two phases [199], viz., frozen phase or fixed points and reversible phase. Thus, shape memory effects have been observed with such polymers as *trans*-polyisoprene (TPI), styrene-butadiene polymer (SB) and segmented polyurethanes (PUs). In these materials, the crystalline soft domains (e.g., crystalline phase of TPI, crystalline polybutadiene segments of SB, and crystalline soft segments of PU) form the reversible phase, with their crystalline melting temperature being the shape recovery temperature (T_s), and hard domains (e.g., cross-links in TPI, styrene blocks in SB, and hard segments of PU) become the fixed points or frozen phases. During the second shaping process, which normally is done at a temperature higher than T_s , frozen phases remain intact. The reversible phases soften above T_s and harden when cooled below T_s .

Basic principles of shape memory behavior of polymers can be best described in terms of their modulus (E)-temperature (T) behavior, as shown in Figure 5.80, where T_s is the crystalline melting temperature of soft segment and T_h is the softening-hardening transition temperature of fixed phase, while T_l and T_u are the typical loading and unloading temperatures, respectively. During the primary processing, such as injection molding, the materials are heated above T_h , where the previous memories are completely erased. In the mold, as the temperature decreases below T_h , fixed phases emerge and the formation is completed at T_s . As the specimen is cooled further below T_s , soft segments crystallize and the material is frozen to its glassy state. The shape of this molded specimen is referred to as the “original shape” for the shape memory experiment.

In the second shaping process (e.g., extension, compression, and transfer molding), if the shape of the specimen is changed by deforming at a temperature T such that $T_s < T < T_h$, this new shape becomes fixed on subsequent cooling below T_s under constant strain. Thereafter on warming to a temperature above T_s , the specimen returns to the original shape giving an exhibition of shape memory of the polymer. The driving force of the shape recovery is the elastic strain generated during the deformation.

A high glassy state modulus (E_g) provides the material with high shape fixity during simultaneous cooling and unloading, while a sharp transition from glassy state to rubbery state makes the material sensitive to temperature variation. Thus, a high elasticity ratio (E_g/E_r)—preferably, a difference of two orders of magnitude—allows easy shaping at $T > T_s$ and great resistance to deformation at $T < T_s$. To satisfy all these properties, systematic designs should be carried out to relate the structural varieties with the properties. While the stress-strain-temperature behavior of the material, as explained above, is of basic importance with regard to shape fixing and shape memory effect evaluations, the shape memory element is often subjected to cyclic deformation, such as for an actuator. Hence the cyclic characteristics are also of practical importance in evaluating the durability of the shape memory element.

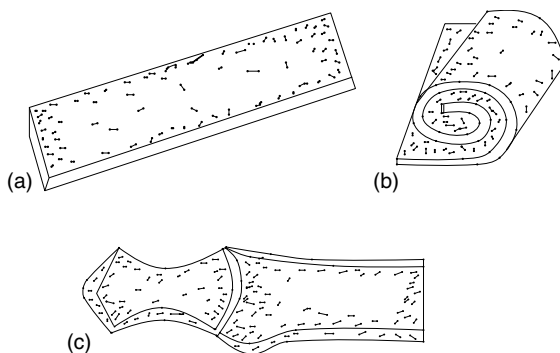


FIGURE 5.79 Illustration of shape memory behavior of a commercial shape memory polymer Veriflex™ (CRG Industries). (a) Coupon of Veriflex having a rectangular memory shape. When heated above its transition temperature, it becomes elastic and can be manipulated into different shapes such as (b) and (c) and then cooled to maintain the new shape in a rigid state. When reheated above its transition temperature, it returns to its memorized shape.

As compared to metallic compounds used as shape memory materials, shape memory polymers have low density, high shape recoverability, easy processability, and low cost. Since the discovery by Mitsubishi in 1988, polyurethane SMPs have attracted a great deal of attention due to their unique properties, such as a wide range of shape recovery temperatures (-30°C to 70°C) and excellent biocompatibility, besides the usual advantages of plastics. A series of shape memory polyurethanes (SPMUs), prepared from polycaprolactone diols (PCL), 1,4-butanediol (BDO) (chain extender), and 4,4'-diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI) have recently been introduced [200–202].

SMPUs are basically block copolymers of soft segments, which are polyols, and hard segments built from diisocyanates and chain extenders (see Figure 4.31). Depending on the types and compositions of soft and hard segments, and preparation procedures, the structure-property relationships of SMPUs are extremely diverse and easily controlled, and hence shape recovery temperature can be set at any

temperature between -30°C and 70°C , allowing a broad range of applications. They can be molded using conventional processing techniques, including extrusion, injection and blow molding, which allow versatility of shaping. In the future, the shape memory effect can be applied to areas like smart fabrics that can control moisture permeability or smart materials with damping capability.

Until the present time, most SMPUs have been prepared from linear PUs, which have physically cross-linked segments. However, these linear SMPUs cannot endure repeated changes in shape memory. In fact, some studies have found that the shape retention and shape recovery of SMPUs decrease dramatically after the first cycle [200]. To improve cyclic shape memory retention and shape memory recovery, SMPUs have therefore been chemically cross-linked by excess MDI or by glycerin [203].

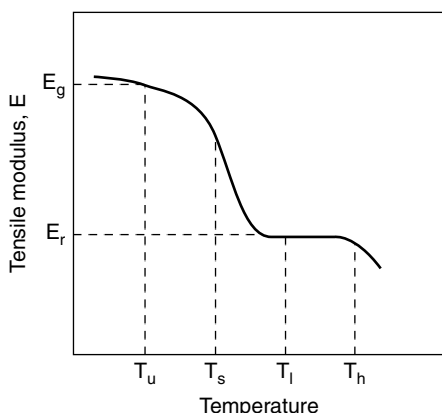


FIGURE 5.80 Typical modulus-temperature curve of a shape memory polymer. (After Kim, B. K., Lee, S. Y., and Xu, M. 1996. *Polymer*, 37, 5781. With permission.)

5.16 Microencapsulation

Microencapsulation [204–207] is a process by which small solid particles, liquid droplets, or gas bubbles are enveloped within a second (coating) material for the purpose of shielding them from the surrounding environment and to release at need. Microcapsules range in size between 1 and 1000 μm . (Capsules greater than 1000 μm can be called macrocapsules, and those smaller than 1 μm are termed nanocapsules.) The coating material used to form the capsule may be an organic polymer, hydrocolloid, sugar, wax, fat, or inorganic oxide. Capsules release their contents at a later time by a mechanism appropriate to the application. The four typical mechanisms by which the encapsulated material is released are mechanical rupture of the capsule wall, dissolution of the wall, melting of the wall, and diffusion through the wall [208]. Less common release mechanisms include ablation (slow erosion of the shell) and biodegradation.

Two well-known examples of microencapsulated products that depend on shell rupture to release the core contents are the scratch-and-sniff perfume advertisements and the carbonless copy paper. The former have tiny perfume-filled microcapsules coated onto the magazine page so that, when scratched, the shell wall ruptures, releasing the perfume. In the case of carbonless copy paper (see Figure 5.81), the underside of the top sheet is coated with small capsules (1–20 μm diameter) containing a dye precursor (2%–6% solution of a leuco dye in a high boiling organic solvent) which is colorless, but darkens when in contact with an acidic component (such as attapulgite clay or phenolic resin). The top of the lower sheet is coated with this acidic component so that when the capsules break due to high local pressure beneath a pen point in writing on the top sheet, the leuco dye react with the acid sites to give an image on the lower sheet. Initially, a mixture of crystal violet lactone and *N*-benzoyl leucomethylene blue was used as the leuco dye. Subsequently, fluoran and phthalide leuco dyes, as also metal chelate color systems were developed. Solvents used as dye carriers are high boiling ($>200^{\circ}\text{C}$) organic liquids which include benzylated ethylbenzene, benzyl butyl phthalate, isopropylbisphenyl, and diisopropylnaphthalene.

Microencapsulation has been applied widely in the detergent industry. Some powder detergents contain protein reactive enzymes such as protease, encapsulated in a water soluble polymer such as

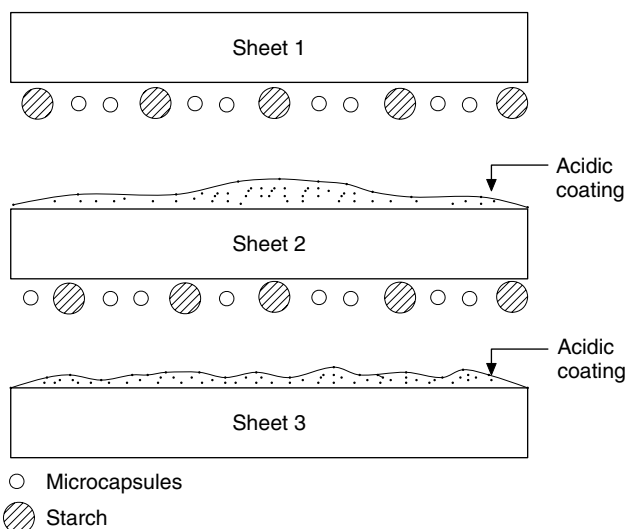


FIGURE 5.81 Cross-section of a three-part business form made with carbonless paper. (After Thies, C. 1989. *Biomaterials and Medical Applications*, Encyclopedia Reprint Series, J. I. Kroschwitz, ed., pp. 346–367. John Wiley, New York.)

polyethylene glycol. Released upon shell dissolution in the washing machine, the enzymes help remove blood stains by attacking the blood protein.

Encapsulated ingredients are used in many packaged baking mixes to delay chemical reactions until proper temperatures are reached. Sodium carbonate is a baking ingredient as it reacts with food acids to produce leavening agents. It is encapsulated in a fat that is solid at room temperature but melts at a temperature of about 125°F. This delays the release of the core material until the proper temperature is reached.

Microencapsulation is a common means of providing sustained release of a medication and is frequently used in the pharmaceutical industry for this purpose. For example, aspirin which provides effective relief for fever, inflammation, and arthritis, can cause peptic ulcers and bleeding in direct doses. Therefore, it is sometimes encapsulated in ethyl cellulose or hydroxypropyl methylcellulose and starch; tablets are produced by pressing together these microcapsules. Instead of being released all at once, the encapsulated aspirin diffuses through the shell producing a slow and sustained release.

A wide range of materials in addition to those mentioned above have been encapsulated. These include pharmaceuticals, vitamins, living cells, catalysts, flavor oils, agrochemicals, adhesives, and water. The advantages of encapsulation are many. Thus unpleasant odor or taste can be effectively masked in a food product, toxic products can be safely handled, sensitive materials can be protected, liquids can be handled as solids, and drug delivery can be controlled and targeted. Microencapsulation has thus found increasing applications in many areas. Usually organic polymers are employed as shell materials. Waxes and fats also find use, especially in food and drug applications for which the U.S. Food and Drug Administration specifications are to be met.

5.16.1 Processes for Microencapsulation

Many processes for making microencapsulated product have been reported in the literature. They encompass a broad range of scientific and engineering disciplines. Some are used in high volume applications as in carbonless copy paper, others are in low volume specialty applications; many are used in pilot plant scale.

5.16.1.1 Complex Coacervation

Conceived in the 1930s by Barrett Green at the National Cash Register Corporation, complex coacervation was the first process used to make microcapsules for carbonless copy paper. The process occurs in aqueous media and is used to encapsulate water-immiscible liquids or water-insoluble solid. The substance (liquid or solid) to be encapsulated is first dispersed as tiny droplets or particles in an aqueous solution of a polymer such as gelatin by mechanical agitation. A second water soluble polymer, such as gum arabic, is then added to this emulsion and mixed. As the pH is adjusted to 4.0–4.4 by the addition of acetic acid, there occurs spontaneous formation of two incompatible liquid phases—one phase, called the coacervate, having relatively high concentrations and the other phase, called the supernatant, having low concentrations of the two polymers. If the materials are properly chosen, a complex coacervate preferentially adsorbs on the dispersed droplets (or particles of water-insoluble substance) to form shell cover of microcapsules. The shells are usually hardened, first by cooling to 5°C, and then by cross-linking with formaldehyde or glutaraldehyde. The capsules are isolated and dried, or used directly as an aqueous dispersion. Since with aldehyde cross-linking the shells remain hydrophilic and hence prone to swelling in water, drying may lead to aggregation. Therefore, to reduce hydrophilicity, such capsules are treated with urea-formaldehyde at a low pH (~ 2).

Any pair of oppositely charged polyelectrolytes capable of forming complex coacervate can be used in the above process of encapsulation by coacervation. Gelatin, a positively charged polyion, forms complex coacervates with a number of polyanions, including alginate, polyphosphate, carrageenan and ethylene-maleic acid copolymers. A wide variety of microcapsules containing water-insoluble or water-immiscible

materials can be made by complex coacervation. The capsule size ranges from 5 to 1000 μm with typical loading of 80%–95%.

5.16.1.2 Polymer-Polymer Incompatibility

Microencapsulation based on polymer-polymer incompatibility utilizes the phenomenon that when two chemically different polymers are dissolved in a common solvent (usually organic) they separate spontaneously into two liquid phases with each phase containing one of the polymers predominantly. When a substance (active agent to be encapsulated) which is insoluble in the solvent is dispersed in such a system it is engulfed by the polymer in one of the two phases due to preferential adsorption, resulting in the formation of embryo microcapsules. The coating polymer is then insolubilized by chemical cross-linking or addition of a nonsolvent and microcapsules are separated. The active agents encapsulated are typically polar solids possessing some degree of water solubility and ethyl cellulose is the most commonly used coating polymer. Aggregation of capsules during isolation is often encountered in this type of process.

5.16.1.3 Interfacial and In Situ Polymerization

The first step in all interfacial polymerization processes for encapsulation is to form an emulsion. This is followed by initiation of a polymerization process to form the capsule wall. Most commercial products based on interfacial or in situ polymerization employ water-immiscible liquids. For encapsulation of a water-immiscible oil, an oil-in-water emulsion is first formed. Four processes are schematically illustrated in Figure 5.82. In Figure 5.82(a), reactants in two immiscible phases react at the interface forming the polymer capsule wall. For example, to encapsulate a water-immiscible solvent, multifunctional acid chlorides or isocyanates are dissolved in the solvent and the solution is dispersed in water with the aid of a polymeric emulsifier, e.g., poly(vinyl alcohol). When a polyfunctional water-soluble amine is then added with stirring to the aqueous phase, it diffuses to the solvent-water interface where it reacts with acid chlorides or isocyanates forming the insoluble polymer capsule wall. Normally some reactants with more than two functional groups are used to minimize aggregation due to the formation of sticky walls.

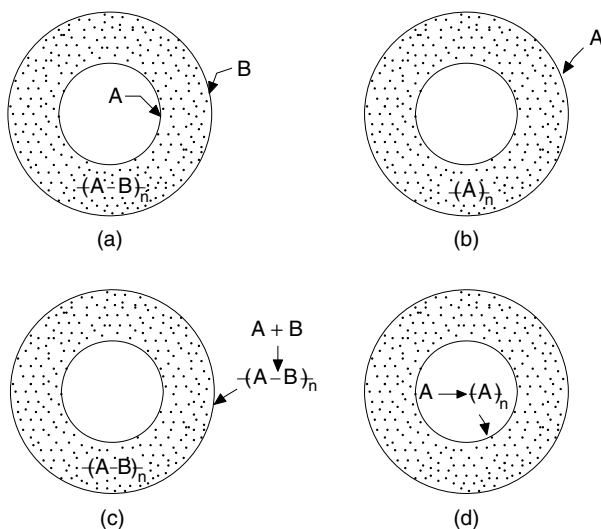


FIGURE 5.82 Microcapsule formation by interfacial and in situ polymerization. A and B are reactants, while— $(A-B)_n$ —and— $(A)_n$ —are polymeric products. See text for explanation. (After Thies, C. 1989. *Biomaterials and Medical Applications*, Encyclopedia Reprint Series, J. I. Kroschwitz, ed., pp. 346–367. John Wiley, New York.)

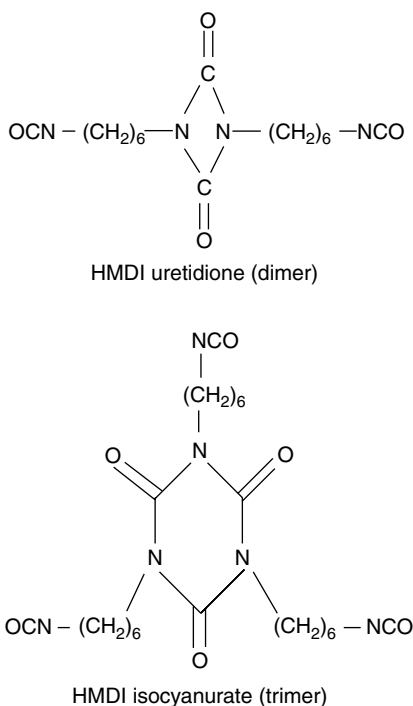


FIGURE 5.83 Chemical structures of HMDI uretidione and HMDI isocyanurate. (After Takahashi, T., Taguchi, Y., and Tanaka, M. 2005. *J. Chem. Eng. Japan*, 38(11), 929. With permission.)

Acid chlorides commonly used include sebacoyl chloride, terephthaloyl chloride, and trimesoyl chloride. The last named acid chloride has three functional groups and hence serves as a cross-linking agent. Among the various isocyanates used, mention may be made of polymeric isocyanates based on *p,p'*-diphenylmethane diisocyanate and other isocyanate adducts based on toluene diisocyanate and hexamethylene diisocyanate. Amines, such as ethylenediamine, hexamethylenediamine, and triethylenetetramine are added to the aqueous phase, the last named amine being a cross-linking agent. A base is added to serve as an acid scavenger if acid chlorides are used.

Microencapsulation by interfacial polycondensation is a useful method to microencapsulate a liquid core material. Especially, polyurea and polyurethane microcapsules have been extensively investigated in various industries [209]. For example, aliphatic hexamethylene diisocyanate (HMDI) and aliphatic ethylene diamine (EDA) have been used to prepare polyurea microcapsules containing insecticide called diazinon [210]. A urea linkage is formed immediately by the reaction between an amine and an isocyanate group (see Figure 4.31), and a polyurea is synthesized by the reaction between an amine with two or more amine groups and an isocyanate with two or more isocyanate groups.

In the presence of a basic catalyst, HMDI can dimerize to HMDI uretidione and trimerize to HMDI isocyanurate (Figure 5.83). Polyurea microcapsules prepared from HMDI uretidione or isocyanurate (by reacting with EDA) are stronger than those obtained from HMDI. Moreover, HMDI uretidione and isocyanurate do not have bad smell like the HMDI monomer. So these may be preferred for the industrial application. The preparation of polyurea microcapsules containing a pyrethroid insecticide by the reaction between HMDI uretidione/isocyanurate and EDA has been reported [211]. In a typical method of preparation, as shown in Figure 5.84, given amounts of insecticide and the mixture of HMDI uretidione/isocyanurate (Desmodur N3400) are mixed and dispersed in water with poly(vinyl alcohol) as a stabilizer (4 wt%) to form oil-in-water (O/W) emulsion to which a given amount of EDA aqueous solution is then added with agitation to facilitate interfacial polymerization. Single cored microcapsules, 0.2–6.0 μm in size, have been obtained by this method in about 98% yield [211].

Figure 5.82(b) represents capsule wall formation by direct polymerization of a monomer (A) such as *n*-alkyl cyanoacrylate at the water-solvent interface. In this case, water is dispersed in a water-immiscible solvent with the aid of an emulsifier and *n*-alkyl cyanoacrylate is added to the solvent phase from where it diffuses to the solvent-water interface and polymerizes to poly(*n*-alkyl cyanoacrylate), forming capsule wall membrane.

In a variation of the above process, a water soluble monomer A is adsorbed on water-immiscible solvent droplets dispersed in the aqueous solution of A and then polymerized to form closed shell structure. For example, cross-linked polysaccharide capsules with diameters ranging from 200 nm to several microns and wall thicknesses of several tens of nanometers have been fabricated by interfacial polymerization of methacrylated *N,N*-diethylaminoethyl dextran (DdexMA) [212]. In a typical method of preparation of DdexMA (see Figure 5.85), a mixture of *N,N*-diethylaminoethyl dextran (Ddex),

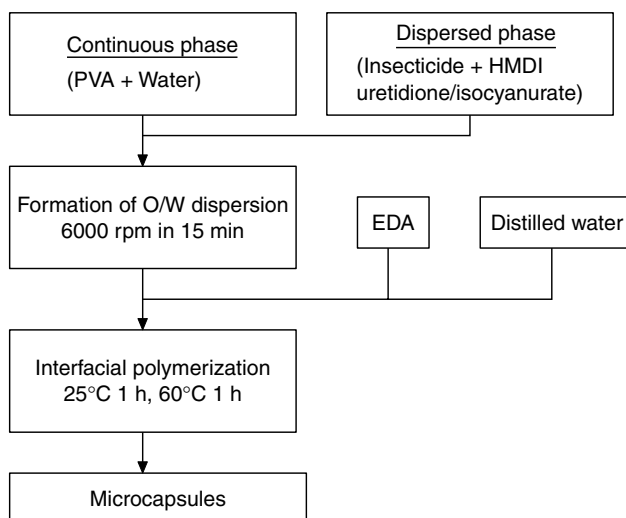


FIGURE 5.84 Flow chart of the process of preparation of polyurea microcapsules. (After Takahashi, T., Taguchi, Y., and Tanaka, M. 2005. *J. Chem. Eng. Japan*, 38(11), 929. With permission.)

methacrylic acid (MAA), and water soluble carbodiimide (1-ethyl-3-dimethylaminopropyl carbodiimide, EDAC) is incubated at 25°C in phosphate buffered saline (pH 7.4) for 24 h. After filtration the synthesized macromonomers are dialyzed in distilled water to remove the excess MAA and EDAC.

In a typical method of encapsulation (see Figure 5.86), droplets of chloroform or chloroform solution of the drug to be encapsulated are dispersed in water containing DdexMA with the help of an emulsifier (e.g., Triton X-100). The polymerization of DdexMA is initiated by the addition of redox initiator $K_2S_2O_8/NaHSO_3$ under nitrogen atmosphere at 40°C. After polymerizing for 8 h, chloroform is

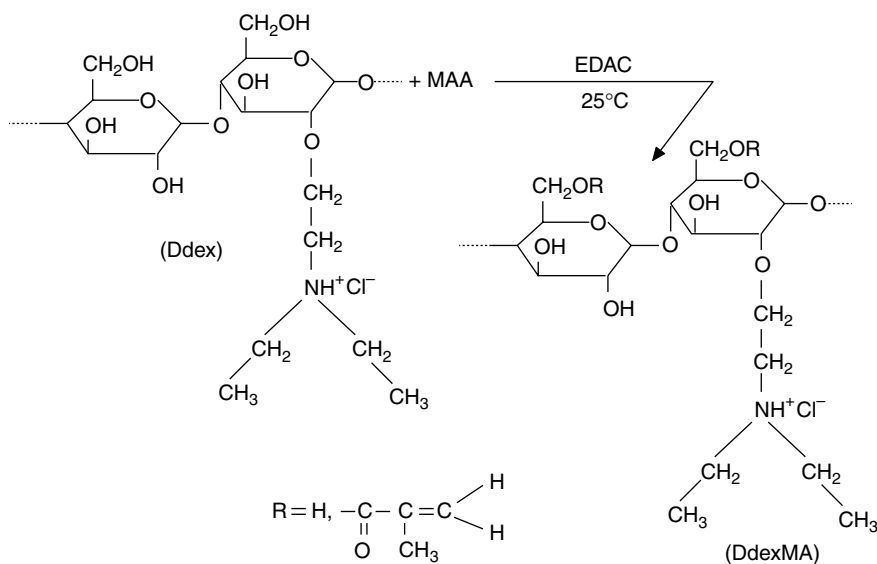


FIGURE 5.85 Synthesis of methacrylated *N,N*-diethylaminoethyl dextran (DdexMA) (see text for description). (After Jiang, B., Hu, L., Gao, C., and Shen, J. 2006. *Acta Biomaterialia*, 2, 9. With permission.)

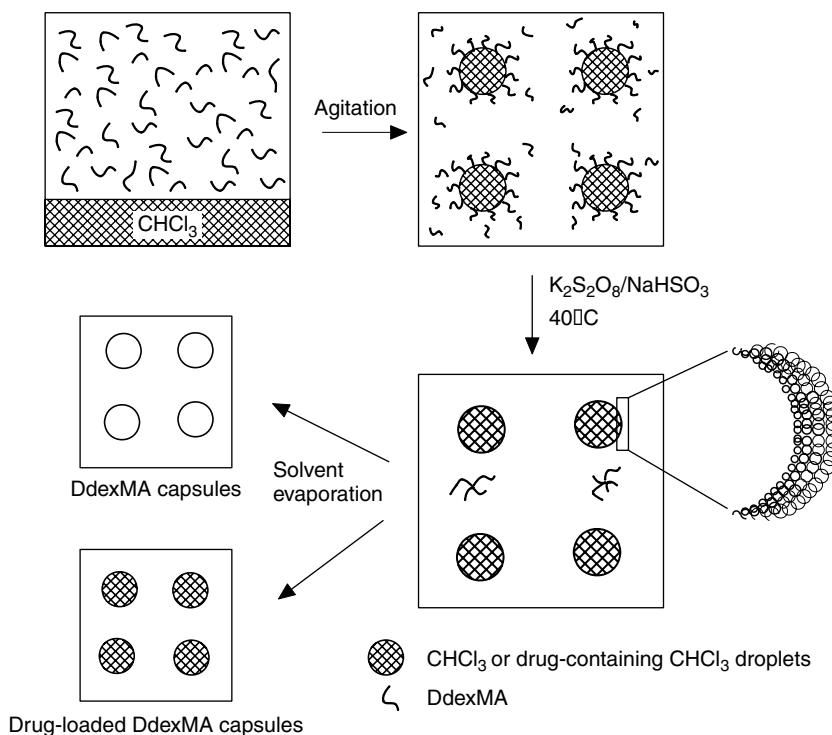


FIGURE 5.86 Schematic description of the process of capsule formation by interfacial polymerization of DdexMA (see text). (After Jiang, B., Hu, L., Gao, C., and Shen, J. 2006. *Acta Biomaterialia*, 2, 9. With permission.)

evaporated to obtain empty DdexMA capsules or drug-loaded DdexMA capsules. The loaded drug can be released from the capsules in a sustained manner.

In the encapsulation process depicted in Figure 5.82(c), polymerization is initiated in the water phase of oil-in-water emulsion. As the molecular size of the polymer increases, it deposits at the water-oil interface where it continues to grow forming a cross-linked polymer capsule wall. In a typical example, methylol urea or methylolmelamine is added to the aqueous phase along with an ionic polymer. The pH is adjusted to 3.5–4.5 and the mixture allowed to react for 1–3 h at 50–60°C. The ionic polymer in the aqueous phase assists deposition of the aminoplastic at the water-oil interface.

The process represented in Figure 5.82(d) is similar to that in Figure 5.82(c), except that polymerization is initiated in the water-immiscible solvent phase. A vinyl monomer, e.g., styrene, methyl methacrylate, or vinyl acetate, is dissolved in a water-immiscible solvent together with an initiator. The solution is emulsified in water using an emulsifier and heated to initiate free-radical polymerization. The resulting polymer deposits at the solvent-water interface forming the capsule wall.

5.16.1.4 Spray Drying

Spray-dry encapsulation is a low-cost process capable of producing a range of microcapsules in good yield. It is the earliest commercial encapsulation process and has been improved considerably over the years as a means of forming soluble microcapsules, with active agent payloads up to 60 wt%, though 20–25 wt% is more common. Gum arabic, starch derivatives, maltodextrins, hydrolyzed gelatin, and mixtures of these materials with sucrose or sorbitol are commonly used as the water soluble carrier (wall material) for microcapsules, especially those containing food derivatives. While gum arabic produces spray-dried capsules that are dispersible in cold water, hydrolyzed gelatin yields capsules that are soluble in hot as well as cold water.

In the process, the active agent (usually water-immiscible liquid or oil) is dispersed in aqueous solution of the carrier material with the aid of a suitable emulsifier and the resulting oil-in-water emulsion is sprayed into a heated drying chamber where they remain for 30 s or less. The product of this operation is a dry microcapsule powder consisting of small, spherical particles with a typical diameter of 10–40 μm in which the oil phase is dispersed throughout as 1–3 μm size droplets. A small amount of the active agent in the powder, however, remains free or unencapsulated; it can only be minimized but not totally eliminated.

Various waxes, fatty alcohols, fats and fatty acids are also used as coating (carrier) material. In these cases, the active agent is dispersed in the molten carrier (using an emulsifier, if necessary) and the dispersion atomized through heated nozzles into a cooling chamber where the carrier solidifies to form the coating.

5.16.1.5 Fluidized-Bed Coating

Fluidized-bed coating is more suitable for encapsulation of solid particles. It can also be used for liquids, if they are first absorbed on a porous solid. The solid particles to be coated are placed in a coating chamber and suspended by an air stream in a cyclic flow (Figure 5.87) past a nozzle (at the bottom of the chamber) which sprays the liquid coating phase onto the particles. Carried up into the chamber by the air stream, the coated particles dry by evaporation of the solvent, fall back to the chamber bottom to be carried again by the air stream past the spray nozzle and up into the coating chamber. The cycle is repeated until the coating attains the desired thickness.

Though submicron solid particles can be coated by this process, the particles agglomerate to form capsules of 50 μm or more. For example, in the Wurster process of fluid-bed coating [213], the production is limited to finished particle sizes of at least 150 μm diameter. A large variety of coating materials can be used including hydrocolloids, solvent or water-soluble polymers, sugars, waxes, and fats, applied as solutions, dispersions, or hot melts. Increasing emphasis on reduction of volatile emissions has, however, led to the preference for aqueous dispersions of polymers such as ethyl cellulose and acrylic resins.

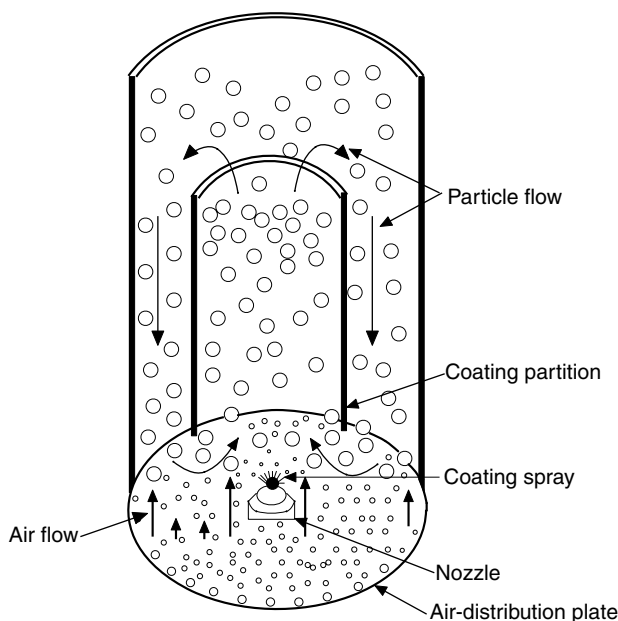


FIGURE 5.87 Schematic of fluidized bed coating chamber (Wurster process). (After Thies, C. 1989. *Biomaterials and Medical Applications*, Encyclopedia Reprint Series, J. I. Kroschwitz, ed., pp. 346–367. John Wiley, New York.)

Coated fertilizers are physically prepared from granules of conventional fertilizers coated with materials that reduce their dissolution rate. Various materials are found to be suitable for coating purposes. The most important of these include wax and sulfur and organic polymers such as polyethylene [214] and polyacrylamide [215]. In a typical process described for coating urea [214], urea prills (size range 0.5–2 mm) are fluidized and sprayed with LDPE solution (10 wt%) in toluene using a dosing pump and atomizing air, followed by drying. The solvent vapors are collected by a tubular condenser. The dissolution of urea in water decreases with increasing coating percentage. This is due to the reduction in the number of pinholes which are the primary path for urea release from LDPE-coated urea.

5.16.1.6 Co-Extrusion Capsule Formation

In this novel encapsulation process, liquid core and shell materials are pumped through concentric orifices in the form of a fluid jet, with the core material flowing through the central orifice and the shell material through the outer annulus. The fluid jet breaks up forming compound drops because of disturbances on the jet surface, the size distribution of the compound drops being thus related to the frequencies of these disturbances. As the compound drop is composed of core fluid encased by a layer of shell fluid, capsules are formed by hardening the shell by appropriate means, such as chemical cross-linking in the case of polymers, solvent evaporation in the case of solution, and cooling in the case of fats or waxes. The size of the capsules formed and the quantity of the core material contained within each capsule depend, in a complex way, on a host of property and process variables, such as density, viscosity, interfacial tension, flow rate and temperature of the fluids, diameters of the inner and outer orifices of the nozzle, and the amplitude and frequency of the vibrational disturbances imparted to the fluid jet. A novel machine vision-based control system (Figure 5.88) under development at the Southwest Research

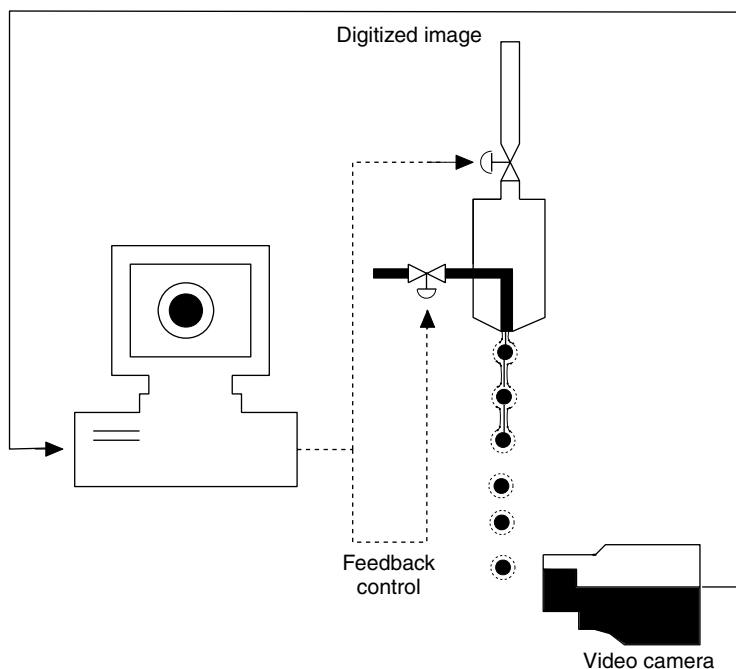


FIGURE 5.88 Schematic of a co-extrusion process of microencapsulation being developed at Southwest Research Institute (SWRI) using machine vision-based control system that allows inflight capsule inspection. The desired capsule size and sphericity are obtained by manipulation of process input variables, such as flow rate, temperature, vibrational frequency, and amplitude via a feedback control loop. (After Franjione, J. and Vasishtha, N. 1995. *Technology Today*, Southwest Research Institute Publications.)

Institute (San Antonio, Texas) allows inflight capsule inspection, while the process input variables including flow rate, temperature, vibrational frequency and amplitude are manipulated via a feedback control loop to obtain desired capsule size and sphericity [207]. Due to the involvement of so many factors and their complex interrelationships, co-extrusion processes are designed and operating conditions determined usually on a case-by-case basis.

5.16.1.7 Other Processes

In addition to the processes described above, there are many other encapsulation processes [Thies, 204] which are in use or are under various stages of development. These include phase inversion in polymer solution, pan coating, solvent evaporation, gelation, electrostatic encapsulation, and vapor deposition.

The phase inversion technique (wet method), in which a polymer is precipitated from its solution with a nonsolvent, can be used to form coatings on solid particles. This technique has been used to encapsulate fertilizers to reduce fertilizer losses and to minimize environmental pollution. For example, polysulfone has been used as a coating for soluble NPK granular fertilizer in controlled-release formulations. In a typical procedure [216], the granular (2–5 mm) fertilizer is added to a 10%–20% solution of polysulfone in *N,N*-dimethylformamide (DMF) and the granules covered with a polymer solution layer are subsequently dropped into a water bath, where the gelation process takes place (the time of the gelation being about 5 s). The coated granules are separated from the water after a maximum of 1 min and then dried in a drier (104°C) to a constant mass. A double coating can be achieved by immersion of the single-coated fertilizer into an adequate polymer solution followed by precipitation in water and drying.

The polymer concentration in the film-forming solution has influence on the physical properties (porosity) of the coatings and the release rate of nutrients from coated granules. Thus for polysulfone-coated NPK fertilizer with coating having 38.5% porosity (prepared from 13.5% polymer solution) 100% of NH_4 was released after 5 h test, whereas only 19.0% of NH_4 was released after 5 h for the coating with 11% porosity [216].

In the pan coating process, a coating material is sprayed onto a particulate ($\geq 800 \mu\text{m}$) mass tumbled in a mixer, forming coated particles. The process is used by the pharmaceutical industry to produce controlled-release products.

In solvent evaporation, the active agent is dispersed or dissolved in a water-immiscible and volatile solvent (such as methylene chloride), and the mixture is dispersed in water allowing evaporation of the solvent to produce microspheres that can be isolated. The technique has been used in the pharmaceutical industry to produce injectable microspheres.

The gelation technology employs chemical interactions to cause liquid droplets to gel, forming microcapsules or microspheres. This technique is used by the pharmaceutical industry to encapsulate active agents and also to immobilize live cells and organisms. In one process, live cells are first entrapped in gel matrix beads produced by the reaction of sodium alginate with calcium ions. The outer layer of the beads is then hardened by treatment with a polycation to form a polyelectrolyte complex, while the interior of the beads is solubilized by treating with sodium nitrate to form a soluble complex.

In the electrostatic encapsulation process, a core material and an immiscible liquid coating phase are converted into oppositely charged aerosols so that the core phase (having higher surface tension) is surrounded by a shell of the coating phase, which is then hardened by a suitable means, forming small microcapsules.

Coating by vapor deposition has been used to form microcapsules, the coating being done on solid particles. The latter may be droplets of frozen liquid or liquid encapsulated by some other process and the vapor deposition may be caused by pyrolysis of di-*p*-xylylene in vacuo [see Poly(*p*-xylylene), Chapter 5]; the reactive *p*-xylylene radical formed by the pyrolysis polymerizes on the solid particles to be encapsulated, forming a thin coating of poly(*p*-xylylene).

5.16.2 Applications

By far the single largest application of microcapsules is in carbonless copy paper used to make multipart business forms. The principle on which the carbonless paper is based is illustrated by the three-part business form depicted in Figure 5.81, which shows the bottom and/or top faces of the sheets coated with a layer of microcapsules and the acidic component, respectively. The capsules and the acidic material may also be coated on the same side and the product is then called self-contained carbonless copy paper.

Small size microcapsules on the paper give sharper image, but are less easily broken by a normal writing instrument. In practice, the upper size limit is ca 20 μm and the lower ca 1–2 μm . Multipart business forms contain up to seven sheets, i.e., one original and up to six copies. For optimum color formation in such a form, sizes of 3–6 μm are recommended.

Another application of microencapsulation in graphic arts is the Sanders light-sensitive imaging system, illustrated in Figure 5.89. Here the top of a paper sheet is coated with microcapsules containing a light-sensitive monomer, a photoinitiator, and a leuco dye. As a pattern or object is imaged on the sheet by a light source, the monomer in those capsules that are exposed to light polymerizes, causing the capsules to solidify (harden), while the liquid in the unexposed capsules remain unchanged. The exposed sheet next passes through a set of rollers whereupon the unexposed capsules collapse and release the dye, thereby forming an image. Color images result from the use of three different dye precursors and three different sensitivities in three different capsules. This technology can be used to reproduce color pictures and documents.

Microencapsulation is common in pharmaceutical industry, particularly when sustained release of a medication is required. Ethyl cellulose is a common coating material. Most capsules are formed by solvent evaporation, polymer-polymer phase separation, or fluidized-bed coating process. Common examples of encapsulated drugs include aspirin, acetaminophen, ampicillin, and potassium chloride. Orally administered capsules serve to conceal an unpleasant taste and reduce gastrointestinal irritation that can be caused by oral unencapsulated drug.

Prolonged release formulations injected intramuscularly, subcutaneously or intravenously and targeted to specific body sites are based on small microcapsules with polylactide or lactide-glycolide copolymers used as wall materials. Some examples of formulations, including those at various stages of clinical trials, are microencapsulated fertility-control drug, luteinizing hormone-releasing analogue, and chemotherapeutic agents.

A number of food additives and ingredients are available in encapsulated form, which include active agents such as citrous flavors, citric acid, ascorbic acid, spice extracts, and vegetable extracts. Encapsulation serves to enhance stability, reduce loss by volatilization and oxidative degradation, increase shelf-life, and impart better handling properties. Water-soluble carriers in common use for food additives are gum arabic, modified starches, maltodextrins and hydrolyzed gelatins. Encapsulation

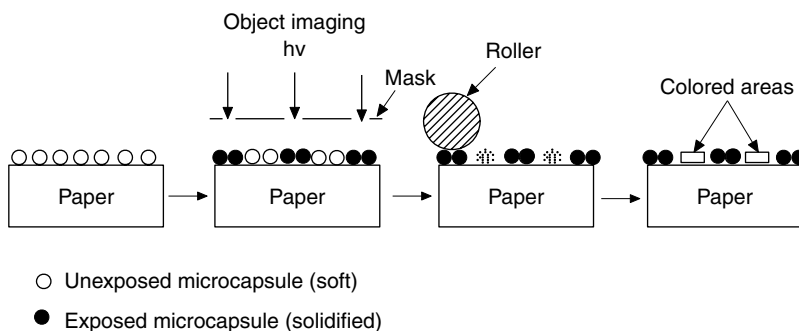


FIGURE 5.89 Mechanism of Sanders imaging system. (After Thies, C. 1989. *Biomaterials and Medical Applications*, Encyclopedia Reprint Series, J. I. Kroschwitz, ed., pp. 346–367. John Wiley, New York.)

is done by extrusion, for which coating formulations are prepared as concentrated solutions. Capsules obtained by extrusion are larger than those obtained by spray drying. Treatment of the capsules with cold and hot water is required for the release of the active ingredients.

Common water-insoluble carriers for food ingredients are low-melting, hydrogenated vegetable oils, e.g., cottonseed or soybean oil. Solid ingredients are coated by the Wurster air suspension process, while liquid ingredients are encapsulated by spray chilling or spray cooling. The capsules are heated above the melting point of the carrier to release the active agents.

Encapsulation of pesticides and herbicides serves to prolong effectiveness and reduce oral toxicity, dermal toxicity, and phytotoxicity, besides concealing any objectionable odor. There are many commercial examples of encapsulated pesticides and herbicides, some of which are methyl parathion, diazinon (highly effective against cockroaches), thiocarbamate herbicides, fonofos (soil insecticide), methoprene (mosquito-growth regulator), pyrethins (effective against crawling insects, e.g., cockroaches), and warfarin (rodenticide). All these products are encapsulated by interfacial or in situ polymerization.

5.17 Polymer Nanocomposites

Nanotechnology is one of the evolving and promising technologies for the new millennium. It is believed to harbor the potential to become a key technology, especially since two different promising major approaches can be observed in the field—first, miniaturization beyond the micrometer (10^{-6} m) size to nano (10^{-9} m) size (which is about 10,000 times finer than a human hair) and second, the exploitation of new effects that arise from nanostructured materials.

A nanocomposite material can be defined as one that consists of two or more different material components, at least one of which has a dimension (i.e., length, width, or thickness) below 100 nm. There are many types of nanocomposites presently under research and development including polymer/inorganic particle, polymer/polymer, metal/ceramic, and inorganic-based nanocomposites. However, the first named one, commonly called polymer nanocomposite (PNC) and defined as the combination of a polymer matrix resin (continuous phase) and inclusions having at least one dimension less than 100 nm, is the only type of nanocomposite to date that has seen any significant commercial activity.

PNCs have emerged as a very efficient strategy to upgrade properties of synthetic polymers, exceeding largely the performance of the conventional fiber- or mineral-reinforced polymer composites. One additional advantage is that relatively small amounts of filler, typically 2–10 wt%, are required as a result of the nanometric scale dispersion of the filler in the matrix. They therefore avoid many of the costly and cumbersome fabrication techniques common to conventional composites. Instead they can be processed by techniques like extrusion, injection molding, and casting normally reserved for unfilled polymers. Furthermore, they are adaptable to films, fibers, as well as monoliths. Because of the small amount of filler used in PNCs, nanocomposite plastic parts offer a 25% weight savings on average over highly filled plastics.

One of the most promising PNC systems is the one based on organic polymers and inorganic clay minerals with layered structure, which belong to the general family of 2:1 layered silicates. Compared to their micro and macro counterparts and the pristine polymer matrix, polymer-clay nanocomposites (PCNs) exhibit higher tensile strength and moduli, lower thermal expansion coefficients, lower gas permeability, greater swelling resistance, enhanced ion conductivity, and greater thermal stability and flame retardance. Moreover, since the length scale involved minimizes scattering, all these favorable properties can be generated without losing transparency. For nanocomposites, therefore, one could also use the term: composites with transparent fillers.

The nanoscopic fillers, as mentioned above, have at least one characteristic length that is of the order of nanometers. Uniform dispersion of these nanoscopically sized particles or nanoelements can lead to ultra-large interfacial area between the constituents (approaching $700\text{ m}^2/\text{cm}^3$ in dispersions of layered silicates in polymers) and also to ultrasmall distance between the nanoelements (approaching molecular dimensions at extremely low loadings of the nanoparticles).

Considering, for instance, a system containing 1 nm thick plates, 1 μm in diameter, the distance between plates would approach 10 nm at only 7 vol% of plates [217]. The behavior of PNCs can be rationalized as follows. The proliferation of internal inorganic-polymer interfaces means the majority of polymer chains reside near an inorganic surface. Since an interface restricts the conformations that polymer molecules can adopt, and since in PNCs with only a few volume percent of dispersed nanoparticles the entire matrix polymer may be considered as nanoscopically confined interfacial polymer, the restrictions in chain conformations will alter molecular mobility, relaxation behavior, and the consequent thermal transitions such as glass transition temperature of the composites [217].

The dimensions of the added nanoelements also contribute to the characteristic properties of PNCs. Thus, when the dimensions of the particles approach the fundamental length scale of a physical property, they exhibit unique mechanical, optical and electrical properties, not observed for the macroscopic counterpart. Bulk materials comprising dispersions of these nanoelements thus display properties related to solid-state physics of the nanoscale. A list of potential nanoparticulate components includes metal, layered graphite, layered chalcogenides, metal oxide, nitride, carbide, carbon nanotubes and nanofibers. The performance of PNCs thus depends on three major attributes: nanoscopically confined matrix polymer, nanosize inorganic constituents, and nanoscale arrangement of these constituents. The current research is focused on developing tools that would enable optimum combination of these unique characteristics for best performance of PNCs.

5.17.1 Preparation of Polymer Nanocomposites

Clay minerals have a layered structure with unit layers about 1 nm thick and sizes ranging from several nanometers to several micrometers. Montmorillonite (MMT) is a clay most commonly used as nanoparticle reinforcement in PNC preparation. It is a crystalline 2:1 layered silicate clay mineral consisting of several hundred individual nanoscale layers held together by electrostatic forces. Its platelets consist of octahedral aluminum sheets sandwiched between two tetrahedral silica sheets. As there are also some magnesium cations (Mg^{2+}) replacing some of the aluminum cations (Al^{3+}), the layers have a net negative charge which is balanced by hydrated inorganic cations positioned in the spacing (galleries) between the aluminosilicate layers [217].

The two main morphologies that are found in PNCs are intercalated morphology and exfoliated morphology (see Figure 5.90). The best performances are commonly observed for the exfoliated nanocomposites. However, the two extreme situations can coexist in the same material. In the intercalated morphology, the polymer chains are located between the clay nanolayers and though the layer spacing may be increased (the amount of separation being determined by the thermodynamic interactions of the clay layer, the cations residing between these layers, and the matrix polymer), the attractive forces between the nanolayers cause them to be in regularly spaced stacks or tactoids.

On the other hand, in exfoliated morphology, individual clay layers are delaminated and dispersed, regularly or disorderly, in the polymer matrix. The objective of exfoliation in PNC fabrication, however, is to uniformly disperse and distribute the layered inorganic (initially comprising aggregates of the nanolayers) within the polymer. In a fully exfoliated morphology (true exfoliates), the individual nanolayers are uniformly (randomly) dispersed throughout the composite. The achievement of full exfoliation in PNC fabrication, i.e., transformation of an initially microscopically heterogeneous system to a nanoscopically homogeneous system, is the goal of many research activities because of the good effect it has in exhibiting new and improved performance properties of the nanocomposites.

The main techniques that can be used to prepare polymer/clay nanocomposites are: (a) melt mixing the layered clay with polymer, (b) mixing the layered clay with solution of polymer followed by solvent removal, and (c) in situ intercalative polymerization, where the monomer is first intercalated in the clay and subsequently polymerized in situ.

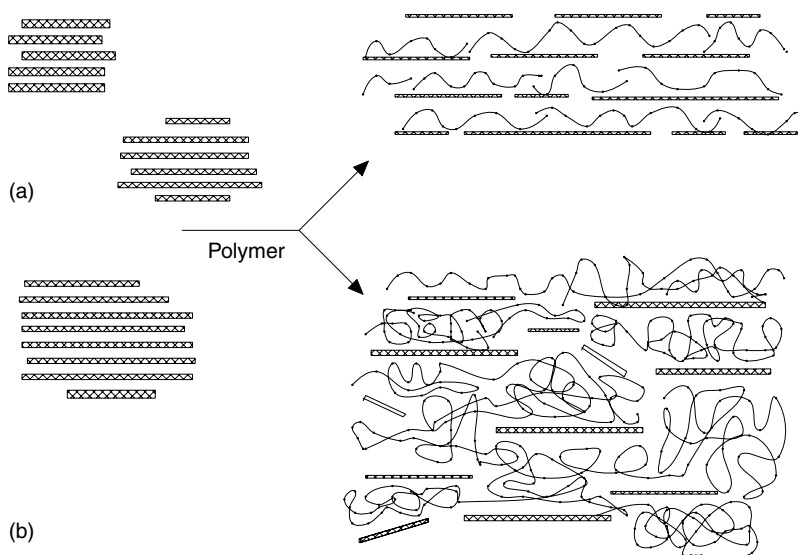
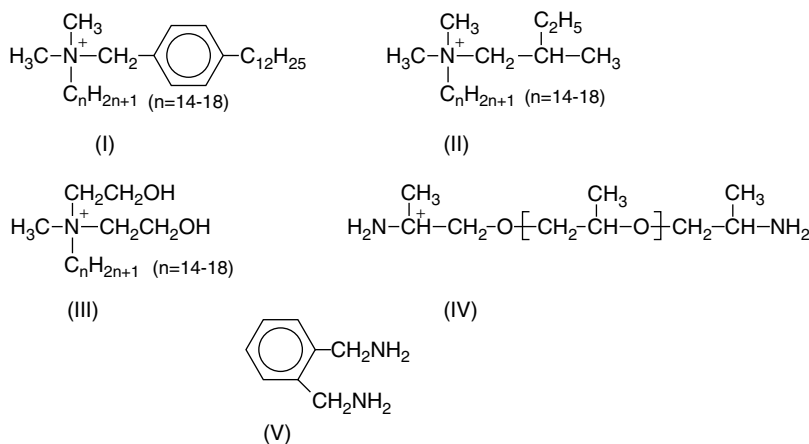


FIGURE 5.90 Schematic presentation of two extremes of composite structures that can be obtained by polymer melt intercalation of layered silicates. The rectangular bars represent individual silicate layers (1 nm thick). (a) Single polymer layers intercalated in the silicate galleries. (b) Delamination (exfoliation) of layered silicates and dispersion in a continuous polymer matrix. (After Giannelis, E. P. 1996. *Adv. Mater.*, 8(1), 29. With permission.)

Natural, unmodified montmorillonite-Na (MMT-Na) has cation exchange capacity, typically 80–90 mequiv/100 g. Although some polymers, such as polyethylene oxide or polyvinylpyrrolidone, are of sufficient polarity to be able to directly exfoliate unmodified MMT-Na, organic modification of the layered clay is usually required to render the hydrophilic surface of the clay more hydrophobic and thus more compatible with most polymers, thereby improving the wettability and dispersibility of the clay in the polymer matrix.

The polymer-clay compatibility is usually promoted by an ion-exchange reaction of the interlayer sodium cations with some cationic surfactants, most of which are alkyl amine salts or quaternary ammonium salts, such as dodecylbenzyl dimethyl alkyl ammonium (I) chloride and dimethyl 2-ethylhexyl alkyl ammonium (II) chloride, in which the alkyl group is C_nH_{2n+1} ($n=14-18$). Hydroxylated quaternary ammonium ions, such as methyl bis(2-hydroxyethyl) alkyl ammonium (III) have also been observed [218] to exfoliate the layered clay as easily as quaternary ammonium ions with no polar functional groups. Thus, poly(ϵ -caprolactam) (PCL)-based nanocomposites have been prepared [219] by the method of melt intercalation by mechanically kneading PCL on a two-roll mill at 130°C with MMT organomodified by (II) or (III). The resulting PNC has interlayer spacing (called the d -spacing) 27–28 Å and 30–31 Å, respectively and contains small stacks of intercalated MMT as also exfoliated sheets.

The organic modifier chain length within the silicate galleries of MMT plays a crucial role in determining the dispersion behavior in nanocomposites. Three types of conformation of aliphatic chains between silicate galleries are possible depending on the number of carbon atoms n [220,221], namely, a lateral monolayer (n up to 6), pseudo bilayer ($n=9-12$) and pseudo trilayer ($n=13-18$). No intercalation occurs for pseudo bilayer, while for $n>12$ intercalated hybrids are formed with the gallery height increasing with the increase in chain length. The increasing n value reflects in the enhanced ability to draw polymer chains between the silicate layers and the decrease in van der Waals attractive forces, leading to intercalated or exfoliated dispersions.



Layered clay nanocomposites have been prepared by melt intercalation for a variety of polymers, including polystyrene [221], nylon-6 [222], ethylene-vinyl acetate copolymers [223], polypropylene [224], polyimide [225], poly(styrene-*b*-butadiene) [226], and PEO [227].

Clay-matrix interaction can be improved further by organic cations containing reactive functional groups which react with either the matrix group or the curing agent [228]. For instance, polyoxypolypropylene diamines (IV) with a long molecular chain have been used as a clay surface modifier, while it also acts as intragallery polymerization catalyst and curing agent, producing a large increase in interlayer spacing (46 Å) and a high degree of exfoliation [229]. In another instance, to induce MMT to be highly exfoliated and homogeneously dispersed in epoxy matrix [230], two different organic reagents, dodecylbenzyl dimethyl alkyl ammonium chloride (I) and *m*-xylylenediamine (V), have been used to modify MMT, since (V) has excellent miscibility with (I) and thus provides a compatible and reactive clay surface for the epoxy.

Besides melt intercalation, described above, in situ intercalative polymerization of ϵ -caprolactone (ϵ -CL) has also been used [231] to prepare polycaprolactone (PCL)-based nanocomposites. The in situ intercalative polymerization, or monomer exfoliation, method was pioneered by Toyota Motor Company to create nylon-6/clay nanocomposites. The method involves in-reactor processing of ϵ -CL and MMT, which has been ion-exchanged with the hydrochloride salt of aminolauric acid (12-aminodecanoic acid). Nanocomposite materials from polymers such as polystyrene, polyacrylates or methacrylates, styrene-butadiene rubber, polyester, polyurethane, and epoxy are amenable to the monomer approach.

An emulsion route can also be used to make nanocomposites with some polymers. Thus well-dispersed (exfoliated) PMMA nanocomposites have been synthesized via emulsion polymerization of MMA in a suspension of MMT (unmodified) or MMT modified with 2,2'-azobis(2-methyl propionamide), using sodium lauryl sulfate as the emulsifier and potassium persulfate as the initiator [232].

It should be noted that among the three different methods of PNC preparation mentioned above, the solution method and the in situ polymerization method have only limited applications because neither a compatible polymer-silicate solvent system nor a suitable monomer is always available. Moreover, they are not always compatible with current polymer processing techniques. Among all the methods to prepare PNCs, the approach based on direct melt mixing/intercalation is perhaps the most versatile and environmentally benign.

While polyolefin nanocomposites are commonly prepared by melt intercalation of MMT organo-clays with polyolefins, unmodified or modified with suitable functional groups (e.g., polypropylene with maleic anhydride or hydroxyl groups [233,234], a new promising technique, known as polymerization filling technique has been reported [235]. The process described for making polyethylene nanocomposites consists in anchoring the coordination catalytic complex (MAO/metallocene system) at the surface in the interlayer of the given non-modified layered clay (hectorite, MMT) and polymerizing ethylene from this surface (Figure 5.91). Molecular hydrogen is added as a transfer agent to control the polymer

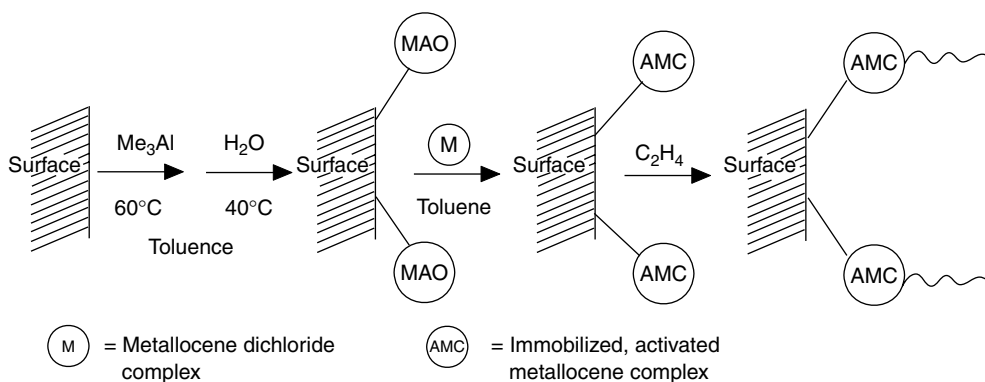


FIGURE 5.91 Schematic presentation of the process of anchoring the coordination catalytic complex, MAO/metallocene, at the surface in the interlayer of layered clay, followed by ethylene polymerization at the immobilized catalyst site. (After Köppl, A., Alt, H. G., and Phillips, M. D. 2001. *J. Appl. Polym.*, 80 (3), 454. With permission.)

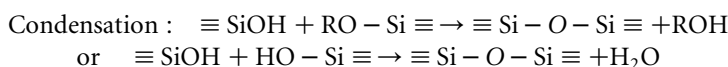
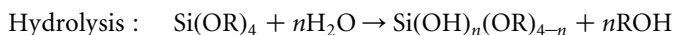
molecular weight, yielding composites with improved tensile properties, characterized by a marked increase in Young's modulus, and improved strain behavior.

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs), due to their unique structure and properties, appear to offer quite promising potential for industrial application [236]. As prices decrease, they become increasingly affordable for use in polymer nanocomposites as structural materials in many large scale applications. In fact, three applications of multiwall CNT have been discussed recently: first, antistatic or conductive materials [237]; second, mechanically reinforced materials [238,239]; and third, flame retarded materials [240,241]. The success of CNTs in the field of antistatic or conductive materials is based on the extraordinary electrical properties of CNTs and their special geometry, which enables percolation at very low concentrations of nanotubes in the polymer matrix [242].

CNFs are intrinsically less conductive than either single-walled CNTs or multi-walled CNTs and CNF composites have the potential for creating inexpensive semiconducting polymers. These composites require a homogeneous dispersion within the polymer. Most well dispersed materials are made by high shear methods like twin screw extrusion [243,244]. However, the aspect ratios of the CNFs are significantly reduced, which leads to decreased mechanical properties and conductivity.

Inorganic-organic hybrid nanocomposites using sol-gel process where the inorganic phase is grown in situ is being actively pursued in many laboratories [245,246]. The main advantage of the sol-gel process, as compared to the traditional practice of mechanically blending the reinforcing fillers into a polymeric matrix, is the subtle control it provides over morphology and/or surface characteristics of the growing inorganic phase in the polymer matrix by control of various reaction parameters like pH, concentration, temperature, etc. Unlike the traditional composites, which have macroscale domain size varying from micrometer to millimeter scale, the organic-inorganic hybrids have domain size varying typically from 1 to 100 nm [247] and so are usually optically transparent, even though microphase separation may exist.

The method of sol-gel hybrid preparation is based on the growth of the inorganic phase by the hydrolysis-condensation of alkoxy silanes (Figure 5.92) like tetraethoxysilane (TEOS) in a solution containing the organic polymer. The reactions can be represented as



So far many hybrids have been prepared in this way using, e.g., poly(vinyl acetate) [248,249], poly(methyl methacrylate) [250], PEO [251], poly(dimethylsiloxane) [252], perfluorosulfonic acid film,

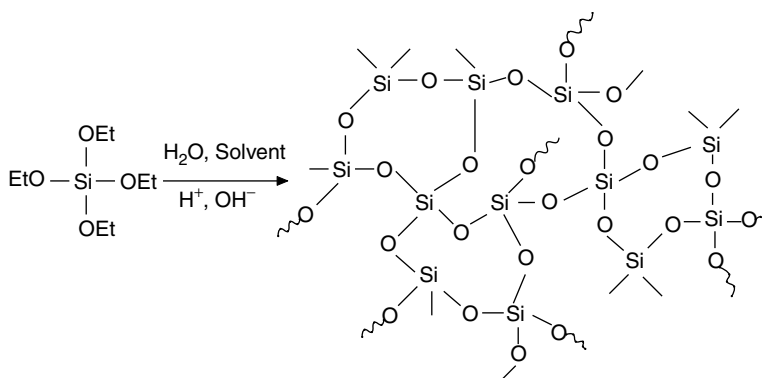


FIGURE 5.92 Overall scheme for the formation of three-dimensional silica network by hydrolysis and condensation of tetraethoxysilane (TEOS). (After Sengupta, R., Bandopadhyay, A., Sabharwal, S., Chaki, T. K., and Bhowmick, A. K. 2005. *Polymer*, 46, 3343. With permission.)

Nafion [253], poly(vinyl alcohol) [254], and polyamide-6,6 [255]. A procedure often followed for polymers soluble in tetrahydrofuran (THF) is to add TEOS to a THF solution of the polymer, followed by addition of water (4 moles based on Si) in the form of 0.15 M HCl or 0.1 M NH₄OH and allowing the reaction to take place. Films are made by casting on an inert substrate such as Teflon and drying under proper conditions. Nafion composite films are made by impregnating swollen Nafion films in alcohol solution of TEOS. The micro- or nanocomposite films made by the sol-gel process are expected to have technological opportunities in important arena of gas-liquid separations, heterogeneous catalysis, electronic materials, and ceramic precursors.

Highly electrically conductive polyaniline/graphite nanocomposites have been made via in situ polymerization of aniline in the presence of exfoliated graphite nanosheets [256]. Graphite nanosheets can be prepared via the microwave irradiation and sonication from expandable graphite powders. In a typical procedure, graphite flakes (80 mesh) are treated with a mixture of concentrated sulfuric acid and hydrogen peroxide (1: 0.08 v/v), washed and dried at 100°C. The resulting expandable graphite powders are irradiated in a microwave oven, thereby obtaining exfoliated graphite (also known as graphite worm), which is then dispersed in 50 wt% alcohol, sonicated for prolonged period, washed and dried to obtain graphite nanosheets.

In a novel procedure reported recently [257], high-performance PNCs have been prepared by growing carbon nanotubes (CNTs) on clay and dispersing the as-prepared CNT-clay hybrid in a polymeric matrix by simple melt blending. This is further elaborated below.

As has been demonstrated, iron, nickel, or cobalt nanoparticles supported on oxides are efficient catalysts for the synthesis of CNTs by chemical vapor deposition (CVD), which has proven to be a cost-efficient way of mass-producing CNTs [258]. Clay has also been used as the support for catalytic CVD growth of CNTs [258a]. While clay platelets are typical two-dimensional (2D) nanofillers for incorporation into polymeric matrices, carbon nanotubes, as one-dimensional (1D) nanomaterials, have also been considered as ideal enhancement fillers for making PNCs because of their extremely high mechanical strength and high electrical and thermal conductivity. For both 1D and 2D nanofillers, homogeneous dispersion in polymeric matrices and strong interactions with the matrices are important issues, which are addressed effectively by using CNT-clay hybrid nanofillers for making composites. This has been demonstrated by using clay-supported iron nanoparticles as a catalyst for the growth of CNTs followed by incorporation of the as-prepared CNT-clay hybrid nanofillers into a nylon-6 (PA6) matrix to make PA6/CNT-clay composites [257].

Figure 5.93 depicts the procedure for making the nanofiller and the polymer nanocomposite by the aforesaid method. Firstly, the sodium montmorillonite (Na⁺ MMT) is modified by impregnation with a

$\text{Fe}(\text{NO}_3)_3$ solution whereby Fe^{3+} ions are intercalated into the layers of MMT. The Fe^{3+} ions are changed to Fe_2O_3 particles by calcination. During CVD growth of CNTs, the Fe_2O_3 particles are reduced to Fe particles in situ, which serve as seeds for the growth of CNTs. The platelets of the clay are further delaminated as the CNTs grow on them, forming a 3D nanostructure consisting of a 2D nanoclay platelet and several attached nanotubes. The obtained CNT-clay hybrid has been directly used as a filler and incorporated into PA6 by melt-blending for the preparation of PA6/CNT-clay nanocomposite [257]. By transmission electron microscopy, the CNTs attached to the clay platelets have been found to be multiwalled with thicknesses ranging from several nanometers to about 20 nm.

The CNT-clay hybrid with its unique structure is expected to be an ideal filler for high-performance PNCs. This has been demonstrated [257] for the PA6/CNT-clay nanocomposite as incorporation of only 1 wt% CNT-clay hybrid is found to improve significantly the mechanical properties of PA6 (see Figure 5.94).

Organic nanofillers are relatively unknown. It is, however, reported that elastomeric nanoparticles (ENP) added to brittle plastics can significantly increase their toughness. Thus phenolic resins have been blended with nitrile butadiene and carboxylic nitrile butadiene ENPs leading to large increase in impact strength and simultaneous improvement in flexural strength and heat resistance [259]. The ENPs are special ultra-fine fully vulcanized powdered rubbers, prepared by a special irradiation technique [259a].

5.17.2 Applications of Polymer Nanocomposites

The only examples of PNCs that have achieved any commercial significance to date are the nanocomposites produced using layered clay minerals (montmorillonite, hectorite, etc.) and carbon nanotubes (CNTs). Polyolefin nanocomposites made via melt intercalation or by the various in situ methods using olefin polymerization catalysts supported on nanofillers are a potentially promising route to new materials for automotive applications. Perhaps the most successful PNC system so far demonstrating dramatic improvement in properties is polyamide (nylon)-6/clay nanocomposite (PA6CN), which shows, as compared with nylon-6, a doubling of the tensile modulus (2.1 vs. 1.1 GPa) and strength without sacrificing impact resistance for products containing as little as 2 vol% of layered clay. In addition, the coefficient of linear thermal expansion is reduced in half (6.3×10^{-5} vs. 13×10^{-5}), a key factor in dimensional stability and an essential factor to manufacture large vehicle parts, while the heat distortion temperature increases to more than 100°C , extending the use of the PNCs to higher temperature environments, such as for under-the-hood parts in automobiles (e.g., timing chain cover for Toyota). PA6CNs are available both as films for packaging and composites for injection molding and other processes.

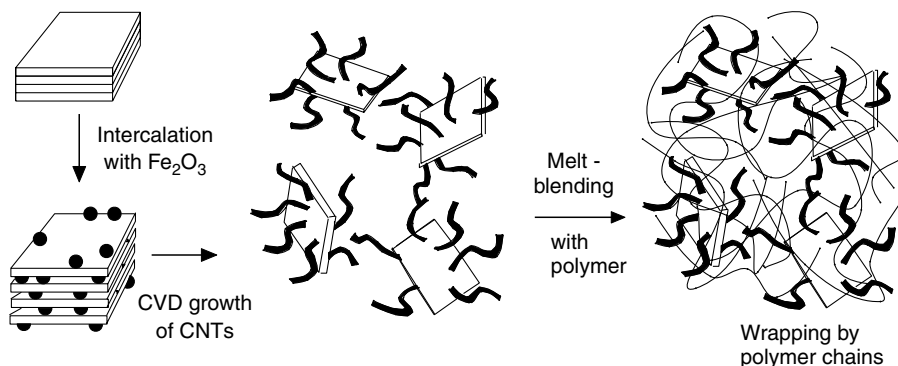


FIGURE 5.93 Schematic presentation of the procedure of growing carbon nanotubes (CNT) on clay particles and incorporation of CNT-clay hybrid filler into PA6 matrix for making PA6/CNT-clay nanocomposite. (After Zhang, W. D., Phang, I. Y., and Liu, T. 2006. *Adv. Mater.*, 18, 73. With permission.)

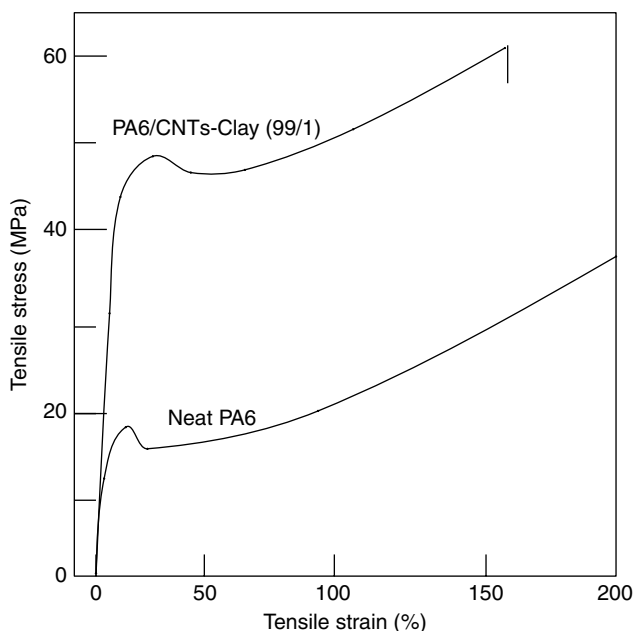


FIGURE 5.94 Stress-strain curves of neat PA6 and its nanocomposite containing 1 wt% CNT-clay nanohybrid. (After Zhang, W.D., Phang, I.Y., and Liu, T. 2006. *Adv. Mater.*, 18, 73. With permission.)

Since the large increase in stiffness and strength is realized with only a small amount of inorganic reinforcement, PA6CNs are much lighter compared to conventional polymer composites, offering a 25% weight saving on average over highly filled plastics and as much as 80% over steel. Using the PNCs only for structurally non-critical parts such as front and rear fascia, cowl vent grills, valve/timing covers, and truck beds could yield several billion kilograms of weight saved per year. This reduction in weight offers to the automotive industry and vehicle users the potential of significant energy savings, which could be further expanded by applications into structural components, interiors, and body panels [235].

The weight advantage of using PNCs in automotive manufacturing could have significant impact on environmental concerns besides many other potential benefits. Thus, it has been reported that wide and large scale use of PNCs by U.S. vehicle manufacturers could save 1.5 billion liters of gasoline over the life of one year's production of vehicles and the corresponding reduction in carbon dioxide emissions would be more than 10 billion pounds [217]. The use of nanocomposites is also expected to improve manufacturing speed and promote recycling.

Even minor loadings of layered clay in PNCs result in substantial reduction in flammability which has been attributed to the build-up of a protective char layer involving the clay [260]. Substantial improvement in the ablative properties of materials due to a similar char formation has also been reported [261]. These properties could lead to the development of novel fire resistant composites without the use of halogenated compounds that have negative environmental impact and hydrated inorganic oxides that require substantial loading.

It has been found that the platelet nature of exfoliated clays in polymers dramatically reduce the permeability of liquids and gases through the composite. The outstanding combination of this barrier behavior and improved mechanical properties of nanocomposites may eliminate the need for a multipolymer layer design for food and beverage packaging [217] enabling simpler process for polymer recycling. Commercial grades of PA6CN for packaging film are available from Ube and Bayer.

There are a variety of potential applications of carbon nanotube (CNT) reinforced thermoplastic composites in automotive industry and systems involving electrostatic dissipation (ESD) and EMI.

Unlike conventional carbon fillers which require high loading to provide conductivity to thermoplastics, leading to considerable deterioration in physical properties, CNT is able to provide conductivity to the composite at very low loading levels. For example, the loading requirement of CNT for electrostatic painting operations is stated [262] to be as low as 2%. CNTs have thus been commercially exploited to assist in the electrostatic paintability of automotive components molded from polyphenylene oxide/polyamide (PPO/PA) alloys. Being produced commercially by Hyperion Catalysts International, the CNTs are 10 nm in diameter and have an average of eight layers of graphite in the tube wall.

Other potential applications of PNCs include layered clays in elastomers for asphalt modification [263] and for tire applications (low air permeability) [264], and layered clay nanocomposites with epoxy [265], unsaturated polyesters [266], vinyl esters [267], and polyurethanes [268] for coatings and composites.

5.18 Wood–Polymer Composites

Wood–polymer composites (WPCs), variously known as wood–plastic composites, wood fiber–plastic composites, and green composites, are a new group of materials that are generating interest in many applications. [Here WPCs are defined as composite materials that contain wood (in various forms) and thermoplastic polymer and do not include wood flour–thermoset plastics like bakelite and particleboard products such as medium density fiberboard.] WPC products use a range of polymers such as polyethylene, polypropylene or polyvinyls in various proportions along with wood or other natural fibers to produce profiles or molded objects with the structural integrity and workability of wood and the durability of polymers. While wood flour or waste wood is mainly used as a cost-cutting alternative to mineral fillers like talc and calcium carbonate, plant fibers like flax, hemp and kenaf are currently being evaluated as environmentally friendly and low-cost alternatives for glass or carbon fibers in engineering composites.

Wood makes an excellent functional filler, but within limits. While the heat used to melt and process plastics does not affect mineral-based fillers, it does affect wood. Therefore, great care must be exercised when using wood as a functional filler. Moreover, wood absorbs moisture, while thermoplastic processing equipment has a near-zero tolerance for moisture.

Plant and wood fibers have a number of advantages over glass fibers. These are: abundant, cheap, renewable, lightweight, non-abrasive, biodegradable, can be incinerated with energy recovery, good mechanical properties as well as good acoustic and thermal insulating properties. The fibers themselves are cellulose fiber-reinforced materials as they consist of microfibrils in an amorphous matrix of hemicellulose and lignin. The hydrogen bonds and other linkages in cellulose provide the necessary strength and stiffness to the fiber, while polymers lignin and hemicellulose are responsible for most of the physical and chemical properties, such as biodegradability, flammability, moisture sensitivity, degradability by UV light etc.

Natural fibers can be classified as: seed fibers (such as cotton), bast fibers (like flax, hemp, jute, kenaf, ramie), hard fibers (like sisal), fruit fibers (like coir), and wood fibers. The chemical composition and dimensions of some common agro-fibers are presented in [Table 5.21](#). The origin of wood fibers can be: sawmill chips, sawdust, wood flour or powder, cutter shavings, pulp or wood residues. As binders for these fibers, both thermosetting (like phenolic, epoxy, polyester) resins and thermosetting matrices [such as polyethylene (LDPE, HDPE), polypropylene (PP), poly(vinyl chloride) (PVC), polystyrene (PS)] can be used. Thermoplastic composites are, however, less expensive to process than thermosetting composites, in addition to their ability to be manufactured into complex shapes.

WPC is claimed to be superior to natural wood in several ways. Its main features can be summarized as follows: (1) the thermoplastic polymer component resists rot and insects, thus providing an inherently longer product life and less maintenance requirement than wood alone; (2) the cellulosic fiber content provides reinforcement, increases the rigidity of the product compared to the polymer component; (3) WPC products can be worked like wood using current tools and fastening techniques; (4) WPC

products can be pigmented during processing for long-lasting color, or painted after installation; (5) WPC products can have virtually 100 per cent recycled content from post-consumer polymeric waste such as milk bottles and grocery sacks and wood fiber scrap from large processors such as furniture or window producers.

5.18.1 WPC Feedstocks

There is no such thing as a typical feedstock that should be used to manufacture a specific WPC and the materials selected depend very much on cost, availability, market value of the product (i.e., low-cost or high-value end of the market) and product performance requirements.

5.18.1.1 Wood

Ponderosa pine, a common species used extensively in window and door manufacture and routinely made into wood floor, is a good overall performer. Other species, such as maple, oak, and many other hardwoods and softwoods can be successfully used. The density of hardwoods can be almost twice that of softwoods and so will result in a heavier product. Moreover, some wood fibers are more durable than others depending on the environmental conditions (wet or dry). Also the modulus is generally higher for hardwoods resulting in a stiffer WPC product.

Wood fiber can be obtained by chemical treatment of the wood (Kraft process, which removes the lignin and low molecular weight waxes) or by thermo-mechanical wood treatment processes, which conserve the lignin and wax content. Wood fiber has a length to diameter ratio between 10:1 and 20:1. Wood flour is available in many sizes, from 20 mesh (coarse) to 400 mesh (extra fine), with 40 mesh being most common. Fine mesh wood flour increases stiffness but reduces impact strength, whereas longer wood fibers contribute to strength but are more difficult to bind with the polymer. For most applications, however, 40 mesh wood flour gives satisfactory performance and ease of processing [269].

Some of the most common sources of recycle wood feedstocks suitable for composites include [269]: (a) primary wood wastes (such as wood wastes from sawmills); (b) secondary wood wastes (generated when wood products, such as furniture, cabinets and doors are made); and (c) post-consumer wood wastes (which can include anything from construction and demolition debris to packaging, crates and pallets). Primary and secondary wood wastes are the key materials used for WPC production in the U.S.A.

TABLE 5.21 Dimensions and Chemical Composition of some Common Agro-Fibers

Type of Fiber	Cellulose (%)	Lignin (%)	Fiber Dimension (mm)	
			Mean Length	Mean Width
Cotton	85–90	0.7–1.6	25	0.02
Flax	43–47	21–23	30	0.02
Hemp	57–77	9–13	20	0.022
Sisal	47–62	7–9	3.3	0.02
Bamboo	26–43	21–31	2.7	0.014
Kenaf	44–57	15–19	2.6	0.02
Jute	45–63	21–26	2.5	0.02
Bagasse	32–37	18–26	1.7	0.02
Deciduous wood	38–49	23–30	1.2	0.03
Coir	35–62	30–45	0.7	0.02

Source: Rowell, R. M. 1998. *Proceedings of the Fourth Pacific Rim Bio-based Composites Symposium*, Indonesia, Nov. 2–5, pp. 1–18.

5.18.1.2 Plastics

As wood degrades at high temperatures, plastics which can be processed below 200°C are generally used. The most commonly used polymers for WPCs using both virgin and recycled material is polyethylene (PE). All polyethylene grades (LDPE, LLDPE, HDPE) are used for the manufacture of WPC. Polypropylene (PP) is also used but requires higher levels of additives to prevent degradation. Poly(vinyl chloride) (PVC) is one of the first plastics to find commercial use in WPC and its use is still growing. The relative quantities of these polymers used in WPC manufacture are PE 70%, PP 17%, and PVC 13%. PE-based products are cheaper and have a higher heat distortion temperature than PVC-based products. But PE-based products have low surface energy which makes painting and post-treatment difficult. This is, however, not the case with PVC.

As for virgin plastics, any recycled plastic that can melt and process below the degradation point of wood (200°C) is usually suitable for manufacturing WPC materials. The choice of plastic, however, depends on the particular application requirements.

5.18.1.3 Compounded Pellets

Compounded WPC pellets are an expensive feedstock option. However, the high initial cost is offset by the fact that these can be molded with less expensive and less complex machines without the need for any additional processing and specialized handling equipment for wood flour. A number of companies have set up plants to produce compounded WPC pellets to sell on to plastics processors. In the compounding process, the filler (wood flour) and additives are dispersed in the molten polymers to produce a homogeneous blend.

5.18.1.4 Additives

Different types of additives are used in WPCs to aid processing operation (e.g., lubricants), to provide processing stability and preservation in long-term service (e.g., heat and light stabilizers) and to improve mechanical properties (e.g., coupling agents).

Lubricants and process aids can be either (a) internal, whereby they act in the resin phase to increase melt flow and throughput, prevent shear burning, and resist melt fracture (by reducing viscosity at high shear rate), or (b) external, whereby they act at the interface between resin and other materials to improve release of the composite, promote dispersion of fillers, resist melt fracture, and/or reduce friction between resin and process equipment.

Primary phenolics (free-radical scavengers) or secondary phosphite (hydroperoxide decomposer) may be used as heat stabilizers for WPC, while light stabilizers commonly used in WPC include UV absorbers (e.g., benzotriazole or benzophenone), radical scavengers or hydroperoxide decomposers, and hindered amine light stabilizers (HALS).

Compatibilizers or coupling agents are polymers containing both polar functional groups that can react or interact with the hydroxyl groups of cellulose and non-polar chain sections that are more compatible with the hydrocarbon chains of WPC polyolefin [270]. Examples of compatibilizers used as WPC additives are maleic anhydride (MAH) grafted polyethylene (PE-g-MAH) and polypropylene (PP-g-MAH), trimethoxyvinylsilane grafted polyethylene and analogous copolymers, polymethylene polyphenylene isocyanate [269], and methylol phenolic grafted polyolefins. The best approach is to use, for example, a grafted PE for a PE base resin, a grafted PP for a PP base resin, and so on. Low molecular weight silanes can be added to the wood filler by spraying or by intensive mixing before blending with the polymer. The compatibilizers promote adhesion and dispersion of the wood component in the polymer matrix, thereby improving the mechanical properties.

Microcellular foamed WPCs are lighter and feel more like real wood [271]. Both extrusion and injection molding have been used to produce foamed WPCs [272], producing materials with a density reduction of approximately 25%.

5.18.2 Manufacture of WPC Products

The processes that can be used for the manufacture of WPC products are compounding, extrusion, injection molding and pultrusion. Drying of wood is an important prerequisite of WPC production since

the moisture content of wood will have a significant effect on the processing and final product quality of WPCs. In some cases, moisture is removed as part of the processing itself (discussed later), while in other cases wood drying is performed separately using additional drying equipment such as preheaters, hot air dryers and rotary tube furnace, the last named device being the most suitable.

5.18.2.1 Compounding

Many options are available for compounding which in many cases is the first stage of the WPC manufacturing process. In batch compounding systems, internal and thermokinetic mixers are used to disperse the wood based filler and additives in the molten polymer to produce a homogeneous blend, while in continuous systems kneaders or extenders are used. The batch process has the advantage that processing parameters (e.g., residence time, shear, and temperature) are easier to control, but has the problem of batch to batch quality difference. The continuous compounding extruder does not have this problem. The raw materials can either be introduced into the extruder simultaneously or the wood fiber added to the molten plastic, a section of the extruder being placed under vacuum to remove moisture from the blend. The compounded material can either be formed directly into an end product or made into pellets for processing in future. A typical WPC pellet compounding line may have a capacity of 4500–9000 kg/h. The pellets can be made with an exact fiber content required for a specific application or, alternatively, highly wood filled WPC pellets can be combined with more resins. The pellets are a boon to manufacturers who do not typically do their own compounding or do not wish to compound in-line, as for example, most single-screw profiles molding companies [273].

5.18.2.2 Extrusion

In order to produce a WPC product by the extrusion process, it is required to first melt the polymer, then mix the molten polymer with the dried wood fiber such that a homogeneous melt is achieved and any remaining moisture can be removed by vacuum venting. The extruder then compresses the homogeneous blend to pass through the die. Various extrusion configurations have been developed for WPC product manufacture [274], some of which are described below.

Single-Screw Extruder (SSE). Equipped with 24:1 or 30:1 ($L:D$) single screw, gravity hopper for material feed, in-line dryer or hopper for moisture removal, and melting/mixing by barrel heat and screw shear, the extruder used for profile extrusion has the advantages of proven technology and lowest machine cost. The SSE system, however, has a number of disadvantages, such as poor mixing, lower output, greater difficulty to vent, and greater risk of burning the wood fiber.

Co-Rotating Twin Screw Extruder (CTSE). This system is commonly used for compounding and profile extrusion in high output applications. CTSE with its high shear is, however, harder to control than the counter rotating system (see below).

Counter Rotating Twin Screw Extruder (CRTSE). This system has parallel or conical, counter rotating twin screws and uses fiber and polymer in same particle size, usually 40 mesh. The extruder is provided with vacuum vent for moisture removal and it uses barrel heat, screw mixing and shear heating for melting and mixing. The system is capable of compounding and generating the high pressure required for profile extrusion. Having shorter residence time and a narrow residence time distribution, the system is also suited to manufacture of PVC windows.

The CRTSE system has the advantages of proven technology, low rpm and low shear. But it has the disadvantages that drying system and size reduction system are required. As the polymer is melted with the fiber, there is a greater risk of burning the fiber, besides venting being more difficult.

Conical Twin Screw Extruder: Conical twin screw extruders are gaining greater acceptance in WPC processing systems. The large screw diameters in the feed section and the increasing compression along the taper of the screws make conical machines well suited for processing materials with low apparent density such as wood fiber. The slimness of the conical screws in the metering section also minimizes the shearing stress on the material which helps the wood fiber remain intact. Moreover, under conditions of identical output, a conical extruder will have more favorable metering section residence times since the

melt will pass the high temperature zone much faster and this will prevent darkening of the WPCs extruded at high temperatures necessary to plasticize the polymer.

Conical Conex[®] Extruder. The conical extruder Conex[®] has a unique design (Figure 5.95) in which conventional single or twin screws do not exist. The material flow is divided into multiple spiral channels with a deep conical rotor ensuring that thermal degradation of polymers and additives do not take place even at relatively high melt temperatures used. Mixing is based on forcing the materials to flow through holes existing at the rotor from spiral grooves, machined onto outer stator surface, into the spiral grooves machined on the inner stator surface, which effectively grind, mix and melt the composite materials being processed in the extruder. The mechanism suits well for composite materials with high filling level of natural fibers and prevents fiber degradation [275]. As the design is self-cleaning, it avoids any stagnation of the flow.

A special feature of Conex[®] extruder not existing in conventional extruders is its ability to grind virtually any cellulose material (such as wood sticks and solid parts, paper, textile, nut shells, straw, etc.) while processing, with adjustable flight clearance between the conical rotor and the stators (typical value being 0.5 mm) and the extruder filling level (starve feeding or full feeding) controlled by the feeding screw rpm vs. the rotor rpm to result in fibers being made on-line of the cellulosic material.

A significant feature of the Conex[®] design is that larger plastics particles will become ground as well as wood particles in the initial part of the extruder. This permits use of feed containing even a limited amount of recycled thermosetting plastics materials, as it will become ground into non-melting plastic dust and act as fillers in composite materials [275]. The possibility of using non-dried wood materials is a notable benefit when comparing with existing technologies. Thus the extruder may be equipped with steam ejection system so that very wet wood can also be used (with the stator temperature at rear set at a high value), the released moisture being ejected as steam from the extruder.

Woodtruder. The woodtruder[™] is a dual extrusion system for wood composite materials made by Davis-Standard Ltd. [276]. It comprises a primary parallel, 28:1 L/D, counter-rotating twin-screw

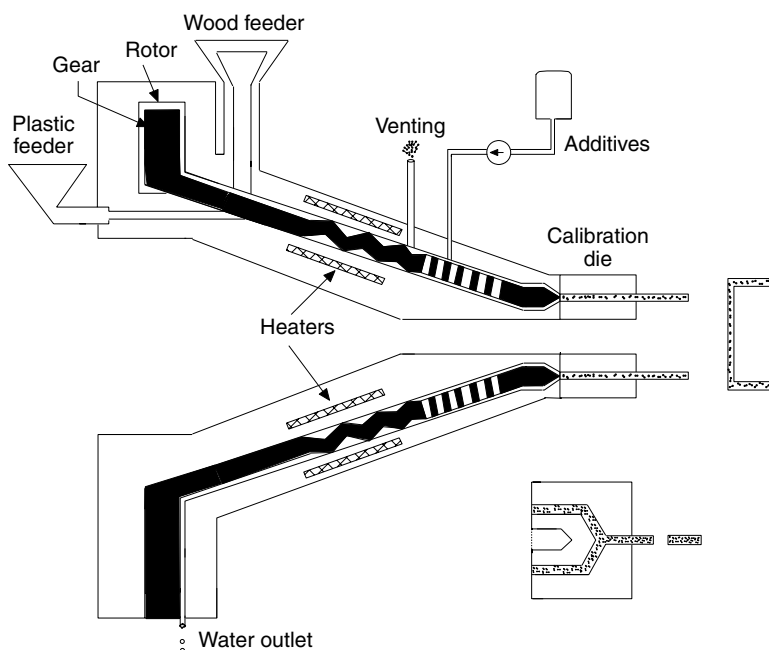


FIGURE 5.95 Schematic layout of Conex[®] wood extruder. (After Mali, J., Sarsama, P., Suomi-Lindberg, L., Metsä-kortelainen, S., Peltonen, J., Vieki, M., Koto, T., and Tisala, S. 2003. *Wood Fiber-Plastic Composites*, A Report dated 31.12.2003, VTT Building and Transport, Finland.)

extruder, a mounted single screw, side-injection extruder, and a crammer feeder that conveys the wood fiber at a controlled rate into the primary extruder. A heating and vacuum venting system in the first section of the primary extruder serve to eliminate moisture from the wood fiber. The side injection extruder, positioned midway through the primary extruder, separately melts and mixes the polymer and then injects the molten polymer at a controlled rate into the primary extruder where the polymer encapsulates the wood fiber, resulting in a thoroughly mixed composite of up to 80% wood fiber. Typical applications include decking, fencing, and window and door profiles. HDPE, PP, PS, PVC, ABS and recycled plastics are used as the plastic component, while the wood component may come from various sources such as wood fiber, peanut shells, rice husks, wood shavings, and jute.

Pultrusion. The schematic of a wood-base pultrusion system is shown in Figure 5.96. The tapered entrance section of the die design is followed by a constant geometry section (of the same dimension as the profile) where the thermoplastic polymer melts and the blend then passes through a cooling section where the polymer hardens. The main requirement of the pultrusion process is that the WPC blend is capable of flowing through the die forming a product of consistent profile [276].

Injection Molding. The WPC injection molding process [277] is similar to conventional injection molding of thermoplastics. The molding material should have good homogeneity and less than 0.5% moisture content. The processing requirements include high rate of plastification, short residence time, and small temperature range of melt.

5.18.3 Properties of WPC Products

In a properly manufactured WPC product, individual wood elements are encapsulated in a continuous plastic matrix which serves to protect the wood from the environment. Therefore care should be taken to stabilize the plastic to UV light and other environmental factors. Moreover, if individual wood elements are not adequately encapsulated, they may absorb moisture, leading to swelling, delamination, and fungal decay [278], though properly manufactured WPC products change very little with humidity variations as the plastic hinders moisture movement in the body. On the other hand, adding wood to plastics produces a beneficial effect by significantly decreasing linear thermal expansion, often by 50 per cent or more [Figure 5.97(a)]. Consequently, WPC products exhibit significantly less mold shrinkage, as compared to virgin plastics [Figure 5.97(b)].

Adding wood to plastics can increase the stiffness sufficiently for certain building applications. As shown in Figure 5.97(c), addition of wood fiber can cause 2–3 fold increase in bending stiffness as compared to unfilled plastics. However, even with these improvements, most WPCs have moduli of elasticity less than half that of solid wood [278].

Other effects of adding wood to plastics can be stated as follows. With increasing content of wood in WPC product, the tensile strength decreases [Figure 5.97(d)], flexural strength increases (up to a maximum), melt index decreases, and notched impact energy increases (while unnotched decreases).

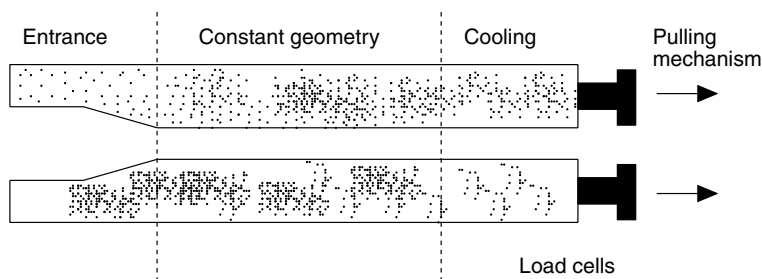


FIGURE 5.96 Pultrusion die design for wood plastic composites. (After WRAP Research Report, 2003. Wood Plastic Composites Study: Technologies and U.K. Market Opportunities. Optimat Ltd and MERL Ltd., The Waste and Resources Action Programme, The Old Academy, Banbury, U.K.)

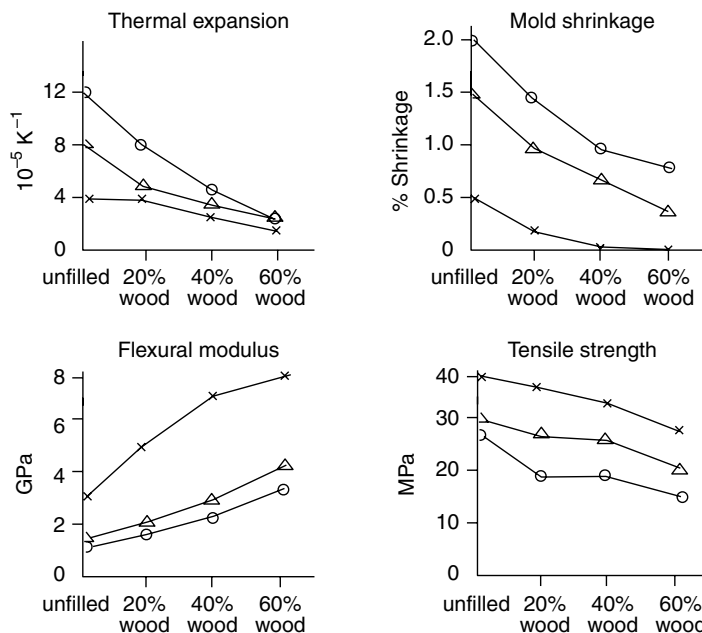


FIGURE 5.97 Effect of plastic type (polyethylene o, polypropylene Δ , polystyrene \times) and wood loading levels on properties of wood plastic composites. (After Chelsea Center for Recycling and Economic Development (CCRED), 2000. Technical Report #19, *An Investigation of the Potential to Expand the Manufacture of Recycled Wood Plastic Composite Products in Massachusetts*, Univ. of Massachusetts, Massachusetts.)

The particle size also has an effect on the property performance of WPC products. For increasing wood particle size in PP-based WPC products, both melt index and tensile elongation increase, notched impact energy increases but unnotched impact energy decreases, and flexural modulus and strength increase for particles smaller than ~ 0.25 mm.

5.18.4 Applications of WPC Products

One of the first commercial use of WPCs was the use of PVC and wood flour for flooring tiles starting in the mid-50s. In 1973, the Sonesson Plast AB Company marketed a wood-PVC composite called Sonwood. It was made by first compounding wood flour and PVC together to make a pelletized feedstock that was then extruded into thin sheets or profiles. Another profile (a shaped product) developed over thirty years ago in Italy called “woodstock” used a mix of about 50% wood flour and 50% PP. Woodstock was extruded in thin sheets, reheated and molded to produce automobile panels for Fiat automobiles. Woodstock is still widely used today.

The WPC industry is, however, only a fraction of a percent of the total wood products industry, though the use of WPCs is increasing at a substantial rate, the greatest growth potential being in building products that have limited structural requirements. Presently, the main WPC product produced in North America is decking. Polyethylene is used in 70% of all products, PVC in 18%, and PP makes out 18%. Other areas of activity are outdoor furniture such as picnic tables, park benches, nature trails/walkways, fencing piers, boardwalks, window and door profiles, automobile components, and pallets [279]. Although WPC decking is more expensive than pressure-treated wood, manufacturers promote its lower maintenance, lack of cracking or splintering [273].

Window and door profile manufacturers form another large industrial segment that uses WPCs. Although more expensive than unfilled PVC, wood-filled PVC is gaining favor because of its balance of

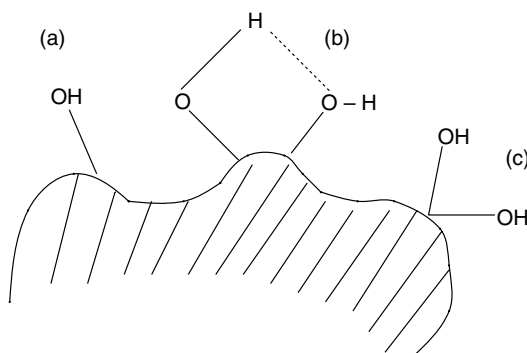


FIGURE 5.98 Surface hydroxyl groups on silica: (A) isolated groups; (B) hydrogen-bonded groups; (C) geminated hydroxyl groups (from the same Si atom). (After Hindryckx, F., Dubois, P., Jerome, R., Teyssie, P., and Marti, M. G. 1997. *J. Appl. Polym. Sci.*, 64, 423, 439. With permission.)

thermal stability, moisture resistance and stiffness [273,280]. Different approaches are being used by several industry leaders to include WPC profiles in their product lines, such as by co-extruding a wood-filled PVC with an unfilled PVC outside layer for increased durability, co-extruding a PVC core with a wood-filled PVC surface that can be painted [281] or co-extruding a wood-filled PVC and a composite with a foamed interior for easy nailing and screwing [280].

In Europe where environmental concerns are a strong driving force, there has been a high growth in the use of natural fiber-reinforced thermoplastics in automotive applications, though the growth is much slower in the U.S.A. Automotive interior applications (decorative, structural, and furniture) for WPC materials are being increasingly promoted and companies such as the Japanese firm Ein Engineering offers technology for production of profiles suitable as decorative moldings and trimmings.

Considerable growth in WPC market is expected in the near future. The phase out of chromated copper arsenate (CCA) treated wood for residential uses such as decks, playgrounds, and fencing (EPA 2002) may also help the growth of the WPC market. WPC sleepers are presently being assessed to replace wooden sleepers for railroad crossties [269]. New building products based on WPC have been developed,

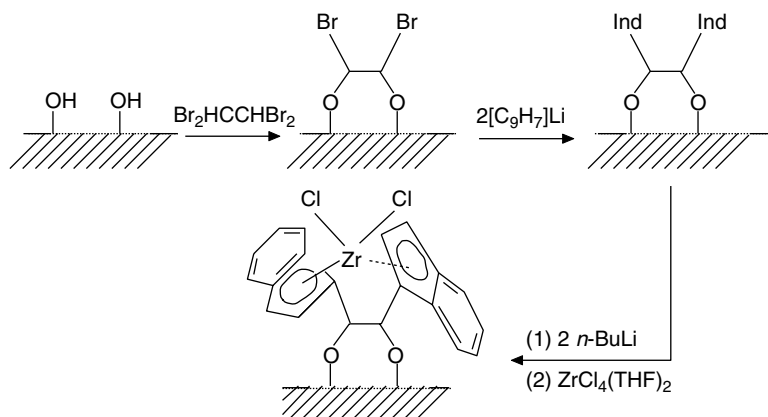


FIGURE 5.99 Schematic of the method of synthesis of a bridge-anchored *ansa*-metallocene. (The indenyl rings are shown in pseudo-racemic orientation as the high isotacticity of polypropylene produced with the catalyst suggests a structural analogy to *rac*-Et(Ind)₂ZrCl₂. (After Soga, K., Kim, H. J., and Shiono, T. 1994. *Macromol. Chem. Phys.*, 195, 3347. With permission.)

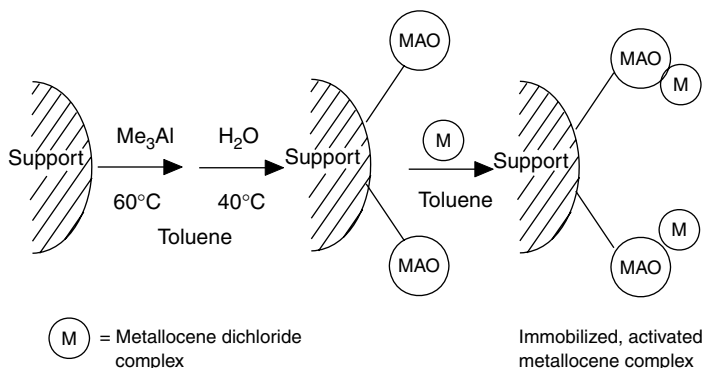


FIGURE 5.100 Synthesis of a heterogeneous metallocene catalyst with immobilized MAO. (After Köpl, A., Alt, H. G., and Phillips, M. D. 2001. *J. Appl. Polym. Sci.*, 80(3), 454.)

for example, preprimed WPC planks for front porches, siding [282] and roof shingles with A class fire rating made from natural fibers and polyethylene.

Advanced WPCs are being investigated to replace treated timber currently used to support piers and absorb the shock of docking ships. Other products include flowerpots, shims (thin washer or strip), cosmetic pencils, grading stakes, tool handles, hot tub siding, and office accessories [273].

5.19 Polymerization-Filled Composites

The industrial interest in filled polymers is steadily increasing as the addition of fillers results in an appreciable reduction of cost and provides the opportunity of producing materials with a new set of selected properties. The preparation of composites by melt blending the polymeric matrix and the filler is a straight-forward procedure but is poorly efficient when the properties of the resulting composites are concerned. In order to overcome these limitations, the polymerization-filling technique has been developed [283,284]. It consists of attaching a Ziegler-Natta-type catalyst onto the surface of an inorganic filler, so that olefin can be polymerized from the filler surface. This allows a very high filler loading (up to 95 vol.%) to be reached together with acceptable mechanical properties. Indeed, the polymer structure and molecular weight (ultrahigh molecular weight polyethylene, UHMWPE) and

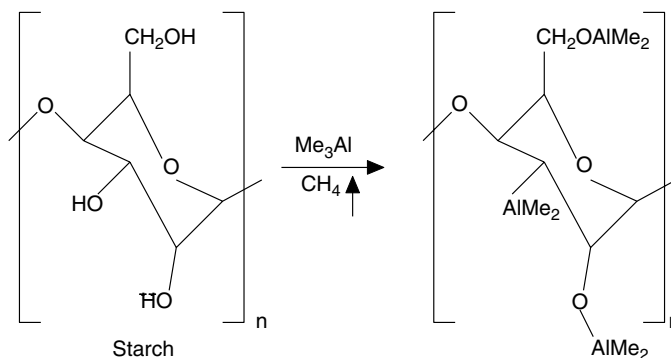


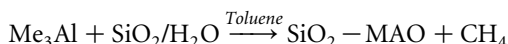
FIGURE 5.101 Reaction of trimethylaluminum with starch in toluene. (After Köpl, A., Alt, H. G., Phillips, M. D. 2001. *J. Appl. Polym. Sci.*, 80(3), 454. With permission.)

the high filling degree are the basis of completely new composite materials that cannot be produced by the standard mixing method [285].

In the early 1980s, UHMWPE was synthesized from a filler-supported catalyst and showed an unusual combination of high stiffness and high impact resistance even for a filler content as high as 60–70 wt%. In spite of these valuable mechanical properties, the interest in this UHMWPE was limited due to very poor processability, requiring either compression molding at high temperature or blending with low-molecular-weight polyethylene so as to reach an acceptable melt viscosity. This latter strategy was used in Russia for producing Norplastic composites [286].

Different methods have been considered to generate active polymerization sites on the filler surface. As a rule, the transition metal compounds have been either merely deposited on the surface and possibly within the pores of the particles, or the organometallic compounds have been reacted with some functional groups, for example, hydroxyls available on the filler surface. As far as silica is concerned, there are three kinds of OH groups on the silica surface, viz., isolated, hydrogen-bonded, and geminated hydroxyl groups (Figure 5.98) [285]. Bridged metallocenes can be covalently bound to silica through reaction of the surface silanols with reactive carbon halide or silicon halide bonds on the ligand bridge. The synthesis of such bridge-anchored *ansa*-metallocene is shown schematically in Figure 5.99. Activities of catalysts based on such surface-bound precursors are reported [287] to be greatly superior to the homogeneous analogs.

In an alternative and significantly more effective procedure [288], trimethylaluminum (TMA) is first attached to silica gel by heating the carrier material with TMA in an inert solvent such as toluene at 60°C until the gas (methane) evolution subsides. The reaction mixture is then cooled down to 40°C and a little amount of water is bubbled through it using a moist argon flow to produce a completely immobilized form of MAO:



Finally, a catalyst precursor (metallocene) is added to the mixture at room temperature, the amount being dependent on the desired Al:Zr ratio. The process is shown schematically in Figure 5.100.

Besides silica, numerous other materials, including alumina, zeolites, clays, and organic polymers have been used as supports for metallocene-based catalysts. In the case of nonreactive particle surfaces, a pretreatment with a reagent bearing functional groups has been used.

Cellulose, starch, and flour are excellently suited for immobilization of MAO because of the presence of OH groups as anchor points (Figure 5.101). The arrangement of the OH groups on the surface possibly serves as a template for the formation of aluminoxane structures that exhibit advantageous cocatalyst properties and the activities of the resulting supported catalysts are typically in the range of 270 kg polyethylene/g Zr-h [288].

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Recycling of Polymers

6.1 Introduction

It is certainly true that plastics left lying around after use do not disappear from view and such post-consumer waste as foam cups, detergent bottles, and discarded film is a visual annoyance. This is because plastics are not naturally biodegradable. However, to consider this a detriment is a questionable argument. Rather, it may well be considered an advantage. This is borne out by the fact that recycling of plastics materials is now an important field in the plastics industry, not just an activity born under environmental pressure.

Although the plastics industry practiced recycling for many years, attention was mainly focused on the recycling of industrial scraps and homogeneous post-consumer plastics, which are easy to collect and reprocess. However, more recently the plastics industry accepted the challenge of recycling of heterogeneous plastics waste based on new technologies of separation and reprocessing. Scientific research, scarcely visible only a few years ago, is now a very active, fast-growing discipline, contributing to the development of newer processes.

According to the type of product obtained from the recycling process and the percentage of the economic value recovered, the following broad classification of recycling technologies can be made (1) primary recycling, the reprocessing of plastics waste into the same or similar types of product from which it has been generated; (2) secondary recycling, the processing of plastics wastes into plastics products with less demanding properties; (3) tertiary recycling, recovery of chemicals from waste plastics; and (4) quaternary recycling, recovery of energy from waste plastics.

The processes mainly used to these ends are: direct reuse after separation and/or modification, chemical treatment or pyrolysis for recovery of monomers and/or other products, and burning or incineration.

Primary recycling is used when the plastic waste is uniform and uncontaminated and can be processed as such. Only thermoplastic waste can be directly reprocessed; it can be used alone or, more often, added to virgin resin at various ratios. The main problems encountered in primary recycling are degradation of the material resulting in a loss of properties as appearance, mechanical strength, chemical resistance, and processability. Contamination of plastic scrap and handling of low-bulk density scrap such as film or foam are additional problems in primary recycling. Primary recycling is widely performed by plastics processors; it is often considered an avoidance of waste rather than recycling.

For post-consumer, mixed plastic wastes (MPW), which are unsuitable for direct use, the industry resorts to secondary recycling methods. There are various technical approaches to secondary recycling of MPW. These include reprocessing based on melt homogenization using specialized equipment; use of ground plastics waste as filler; and separation into single homogeneous fractions for further processing, such as partial substitution of virgin resins and blending with other thermoplastics using suitable compatibilizers.

In tertiary or chemical recycling of plastic wastes, polymers are chemically unzipped or thermally cracked in order to recover monomers or petrochemicals indistinguishable from virgin materials. Thermal cracking procedures offer viable alternatives by utilizing commingled plastics without decontamination. In quarternary recycling, energy content of plastics waste is recovered. In most cases, plastics are burned, mixed with other waste. Incineration of plastics alone creates a number of problems and requires the use of specially designed incinerators.

6.2 Outline of Recycling Methods

Post-consumer plastic wastes can be divided into two different groups depending on their source: (1) mixed plastics from the household waste and (2) plastics from the industrial sectors. The first category involves the medium-/short-life articles that are used in food, pharmaceutical, and detergent packaging, shopping, and others. The majority of these articles are composed of thin protective films: a variety of bottles for soft drinks, food, and cosmetics, sheeting for blisters, strapping and thermoformed trays.

There are basically five different polymers that contribute to the total amount of domestic plastic waste, namely, PE, PP, PS, PVC, and PET. The composition of this MPW can change depending on the regional habits and seasons of a year, and also on the mode of waste collection. A typical composition may be PE 39%, PVC 22%, PET 19%, PS 8%, and PP 12% (by wt).

The collection of plastics wastes always yields a polluted product, and this fact poses the need for the first operation of the recycling process, namely the cleaning of foreign bodies. The machinery required at this stage may be either manual or automatic type, the former being simpler from the standpoint of installation. The operations following the first step of clearing are determined by the type of recycling process to which the material is to be subjected. There are basically two main recycling processes: recycle of heterogeneous MPW and recycle of selected polymers separated from MPW.

A direct solution to disposal of domestic MPW can be the reuse of the heterogeneous mixture by processing through extrusion or injection molding technologies using traditional machineries. However, when MPW is processed, one of the main problems is to find the best compromise between homogenization and degradation. The optimal processing condition must ensure a good dispersion of the materials with high melting point (such as PET) in a continuous phase of molten polymers (such as PVC), avoiding gas bubbles, low-molecular-weight compounds, and cross-linked residues that are formed by thermal degradation. Some possible applications of such molded mixed plastics are injected tiles for paving, and extruded profiles for making structural articles such as benches, garden tables, bicycle racks, fences, and playing facilities. However, because of the incompatibility of the various components in mixed plastics, the mechanical properties of the molded or extruded products are rather poor.

The market of park benches, playgrounds, fences, and so on, cannot absorb, in the long run, the massive amounts of MPW that are produced every year. Hence the possible route to recycling of MPW to obtain secondary materials with acceptable mechanical properties could be to blend them with virgin polymers, or, at least, with recycled homopolymers. For example, experimental results [1] of processing and properties of blends of virgin LDPE and MPW have shown that all mechanical properties, with the exception of elongation at break, are very similar to those of the virgin material if the MPW content does not exceed 50%.

The possibility of using MPW as filler for both LDPE and HDPE has been considered [2] as such an approach, and may offer two important advantages: (1) improvement of the use of huge amounts of MPW that are generated by municipalities and industries; and (2) savings in nonrenewable raw materials and energy, both associated with the manufacturing of the virgin materials that can be replaced by plastics waste. Even if the percentage of plastics waste used as a filler cannot be higher, its common use may absorb sizable amounts of waste.

A widespread solution, in terms of application and market volume, can be the recycling of single materials or homogeneous fractions obtained from a differentiated collection system and/or a separation

process of the mixture. Molded products from single or homogeneous fractions usually show a general performance far greater than that of products from mixed plastics. To obtain single or homogeneous fractions, it is useful to separate the mixed domestic plastics into four fractions, namely, polyolefins, PS, PVC, and PET.

An important preliminary to separation of mixed domestic plastics is the cleaning and selection operation. A simple method to perform this operation consists of a selection platform where a number of trained sorters separate the different types of plastics by visual assessment. Because manual selection is liable to human error, selection platforms may be equipped with detectors such as electronic devices to check the quality of the selected material.

The drawbacks of the manual platforms—which range from high labor cost to the complexity of labor management—may be avoided by resorting to automatic platforms. The machines required for such automation are manifold and the necessity to employ them is related to the quality of the collected material. Essential machines are rotary screen, light-parts separation equipment, heavy-parts separation equipment, and aluminum rejection equipment. All such machines are preliminary to the stage of separation into homogeneous plastic fraction.

Bottles constitute the largest high-volume component of post-consumer plastics and need special attention in reclaim operation. Since 1988, developments in bottle reclaim systems have made recycling post-consumer plastics more efficient and less costly. Municipalities, private organizations, universities, and entrepreneurs have worked closely to develop new collection, cleaning, and sorting technologies that are diverting larger portions of plastics from landfills to recycled resins and value-added end products.

To collect the high volume-to-weight ratio post-consumer plastics economically, truck-mounted compactors have been developed that seem to have the most promising future for mobile collection. They are self-contained and offer, on average, a reduction ratio of 10:1. Simple to operate, compactors accept all types of plastics, including film, and perform equally well with milk jugs and PET bottles as with mixed plastics.

Using compactors for on-board truck densification can thus be a cost-effective part of multimaterial collection programs. Another noteworthy development is that of flatteners and balers, which have also proven cost-effective under certain conditions. An integrated baler developed by Frontier Recycling Systems (USA) is fully automatic and capable of handling the plastic throughput of larger and costlier systems without the corresponding expenditures of space and labor. By producing smaller, high-density bales, it allows for lower transportation costs of recyclables shipped to market.

In keeping with the progress in densification options, efficient sortation systems have also been developed. The Poly-Sort integrated sorting line developed by Automation Industrial Control (AIC), Baltimore, is capable of sorting mixed stream of plastic bottles at a baseline rate of three bottles per second, or 700 kg/h. With expected advances in scanning and detection, the sorting rate of the system could double to 1400 kg/h.

Designed to sort compacted bottles, the Poly-Sort system employs conveyors for singulation, and two devices for color and chemical composition identification. A vibratory conveyor singulates bottles; a read conveyor transports bottles to an ultrasonic sensor that detects their position; a near-infrared system detects the resin type; a camera detects the color of the container; a computer integrates data and makes an identification; air jets divert bottles to the appropriate segregation conveyor or hopper.

The above type of separation is a macroseparation. It may be noted that the methods of separation into homogeneous fractions fall into three groups: molecular separation, microseparation, and macroseparation. Molecular separation is based on the dissolution of the various plastics in selective solvents, a method that is promising but still in the stage of study. Microseparation is a method by which a suspension medium is used to separate plastics with density higher or lower than the suspension medium. Macroseparation, which is the separation of plastics when waste materials are still in initial form, appears to be the most conveniently applicable system, considering the increasing possibilities of automation it offers. The key to this separation process is the development of an efficient detector system that can distinguish between type and quality of different plastics in waste materials.

Different types of detectors have been developed and many are under development. These are based on distinctive physicochemical properties of plastics and employ different techniques such as x-ray, near-infrared spectrophotometry, fluorescence, and optical measurement of transparency and color. Automatic systems consisting of a platform for selection according to plastics topology, a number of identification and detection steps, and adequate checks on the efficiency of separation following detection have been developed. The Poly-Sort system described above is one such example.

Recycle installations take up the separated plastic flakes for further processing. Various elements that normally compose the item to be recycled are caps made of PE, PE with PVC gaskets, aluminum, labels of tacky paper with different types of glue, and residues and dirt that have been added during the waste-collection phase. Various operations that are carried out in a specific sequence because of the problems posed by the type of material are: grinding to ensure homogeneity of the product, air flotation for separation of flakes with different specific weight and removal of parts of labels freed by grounding (such as separation of PVC labels from PET bottle flakes), and finally washing to remove residues. The washing system consisting of a range of equipment that includes centrifugal cleaners, washing tank, settling tank, and scraping machines is part of a know-how of various manufacturers.

The majority of municipal solid waste consists of plastics waste, which is often contaminated with significant amounts of paper. This is not only the case with plastics fraction of municipal solid waste (PFMW), but also with such industrial waste as used packaging materials, laminates, and trimmings. The reprocessing of plastics waste contaminated with more than 5% paper is difficult using conventional plastics processing machinery, and becomes almost impossible at paper levels exceeding 15%. The sorting operation at a municipal plant normally aims at removing the paper component from the light plastics fraction to a level well below 1%. However, this operation has not been quite successful because the material handling side has been difficult and the costs have far exceeded the price of virgin polyolefins.

A simpler solution to the problem of contamination may be to allow for a paper component in the plastics fraction and to use a processing method that can disintegrate the cellulose fibers into small fragments such that they act as particulate fillers in the plastics. Such a method has been developed at Chalmers University of Technology, Gothenburg, Sweden. Known as the CUT-method, the process makes it possible to reprocess both the PFMW and a number of different industrial plastic waste materials contaminated with paper [3,4]. The CUT-method, consisting of a prehydrolytic treatment of the paper component, is an industrially applicable method of reprocessing paper-contaminated plastics waste of various origins.

The main advantage of the CUT-method is that the plastics fraction and the paper component do not need to be separated and the hydrolysis does not degrade the plastics component but reduces the chain length of the cellulose component to a level at which the cellulose fiber becomes extremely brittle and the shear forces generated in normal plastics processing machinery (compounding extruders and molding machines) can easily disintegrate the paper parts into small fibrous fragments. It is the disintegration of the embrittled paper component into an almost pulverized substance that is the key to the success of the method, since this results in greatly enhanced melt flow properties, better homogeneity, and thus in improvement in the mechanical properties of the material [5].

The method of hydrolysis used in the CUT-method offers an efficient and economical way of processing plastic waste, both post-consumer municipal waste and industrial waste, contaminated with a cellulose component. The presence of cellulose gives a desired stiffness to the final product, as studies have shown [4,5]. Such plastics product can be used in several applications, such as artificial wood.

Plastics wastes from industrial sectors concern mostly the medium-/long-life articles, as plastics have played a fundamental role in the exceptional growth of production technology seen during recent years in these sectors, and in particular the automotive industry. Because of the advantage in design and functionality, plastics are now an indispensable part of any kind of car; the amount of polymers employed to build a car has risen to about 20% from a mere 5% in 1973, with a corresponding increase in the quantity of nonmetallic waste during scrapping. The main problem of plastic wastes from all industrial sectors, and in particular the car industry, is the large variety of materials employed to build a single

component or system, for example, a dashboard. This takes place because of the sophisticated and complex mission that the system must perform. The large number of plastics used and the disproportionately high costs in the dismantling of the different plastic pieces of a car represent an intractable waste-recovery problem and thus have a negative impact on the recycling process. As a result of this, only the metallic fraction is recovered, while the plastic materials continue to be eliminated by deposition in refuse dumps.

An alternative approach to the recovery of automotive plastics is therefore to use them as large, easily removable components that offer potential for reclamation as well-characterized individual polymers. Some particularly complex components such as vehicle front- and rear-end systems, exhibit special suitability for manufacture in plastics instead of metals because of their ease of production and assembly. It is generally recognized that improvements in automotive scrapyard economics may be best achieved by the prior removal from vehicles of such large polymeric components and their recycling as well-characterized plastic fractions. For example, plastic fuel tanks of HDPE are now in common use and represent the most common recyclable plastic component. Trials with material recovered from used plastic fuel tanks have shown promising results for the manufacture of new tanks [6].

A concept that is being developed to solve the recycling problems of plastics from industrial sectors, and in particular the car industry, is based on the use of materials of the same family for all components of the plastic systems to be recycled at the life end. This allows an easy and direct recycling of the scraps and the recovery of the whole system. Greater recycling efficiency can be obtained when the following two basic requirements are satisfied: (1) materials compatibility through materials homogeneity, and (2) easier disassembly through planned design. This concept has been first applied to the automotive sector, where the environmental problems have become of primary importance; however, it could be also applied to other products, i.e., appliances and building materials. There are two tasks in developing this concept: to develop new advanced materials in individual categories of polymers and to promote new technologies.

Consider, for example, the automotive industry. Although many polymers are used in cars today, the industry tends to favor more and more polypropylene use due to a large range of properties available. New developments in polyolefin-based materials have thus created a family of polypropylene products with a wide range of physical properties, including the ability to be easily recycled. When utilized by automotive and product designers as a part of a design for disassembly strategy, these compatible materials will yield large subassemblies that can be reclaimed with a minimum of handling [7,8]. In each project, the design incorporates readily identifiable hard point connections between the polypropylene components and the metal automobile subframe. This allows personnel in recycling centers to remove these parts quickly and in large pieces that can be completely reground and recycled. This concept has been applied to car dashboards and interior vehicle components like floor covering, trim, and door panels, as well as bumpers.

Blends of EPDM rubbers with polypropylene in suitable ratios have been marketed as thermoplastic elastomers (TPE), also commercially known as thermoplastic polyolefin elastomers (TPO). These heterophasic polymers, characterized by thermoreversible interaction among the polymeric chains, belong to a broad family of olefinic alloys that can now be produced directly during the polymerization phase, unlike blended TPE and TPO, and various compositions (with various compounding additives) can be formulated which are primarily tailored to meet different requirements of most of car applications. The TPE-based synthetic leather and foam sheets are typical examples.

In order to obtain all-TPE recyclable applications, different assembly techniques have been specifically studied to obtain the basic composite structures [8,9]. The most interesting technique is one that allows simultaneously thermoforming, embossing, and coupling to be obtained in one stage of operation, yielding a foamed synthetic leather bilayer on a rigid support (all TPE based) without adhesives. With new designs for recycling, dashboard, floor covering, and other interior components such as door panels, pillar trim, and rear shelf have been made of the same chemical material (polypropylene) in different forms, thus providing an important aid to the recycling of plastic.

Lead-acid batteries from automotive applications normally have a shorter service life than the car itself. The logistics system for used car batteries is geared to lead recycling. However, the first battery reprocessing step yields not only lead but also polypropylene in a form of the casing fragments. Accordingly, the polymer is available without additional cost. As the casing makes up a substantial part (7%) of the total battery, the quantities of polypropylene obtained are sufficient to warrant the operation of a plastics recycling plant. For example, BSB Recycling GmbH in Braubach, Germany, a subsidiary of Metallgesellschaft AG, operates secondary lead smelter for lead recovery from postuse lead-acid batteries [10]. They process some 60,000 tons of batteries per annum, which accounts for half of the used battery volume to be disposed in the western states of Germany. BSB started to segregate the polypropylene from the battery casings and route it to a separate recycling process as far back as 1984. For the recycling process, a quality assurance system geared to the specific requirements of the applications has been developed and implemented.

Polyolefins and poly (ethylene terephthalate) (PET) are the most frequently recycled polymers obtained from both the domestic and industrial plastics wastes, and as such they have received most attention in the recycling research and technology. PET is one of the largest recycled polymers by volume [11], because it is suitable for practically all recycling methods [12]. Over 50% of the PET film produced in the world is used as a photographic film base. The manufacturers of these materials have long been interested in PET film recovery. An important motivation for this has been the fact that photographic films are usually coated with one or more layers containing some amount of rather expensive silver derivatives.

Silver recovery makes PET-base recovery more economical. In a typical way of operation, PET film recycling is thus coupled with the simultaneous recovery of silver, for example, by washing with NaOH and follow-up treatment. PET-recycling by direct reuse, if the washed PET-film scrap is clean enough to be recovered by direct reextrusion, is by far the most economical process. However, this process is most suited for the recovery of in-production wastes. For customer-recollected PET-film, which may have a higher degree of contamination, other technologies are to be applied.

There exists a hierarchy in PET-film and plastics recycling technologies depending, first of all, on the degree of purity of PET scrap to be handled, and secondly, the economics of the process. For the cleanest PET grade, the most economical process, i.e., direct reuse in extrusion, is self-explanatory. For less-clean PET waste, it is possible to reuse them after a modification step (partial degradation, e.g., by glycolysis) at a reasonably low price. More-contaminated PET waste must be degraded into the starting monomers, which can be separated and repolymerized afterwards, of course at a higher cost.

Polyethylene films from greenhouses, although highly degraded by UV radiation, are recycled by various means leading to manufacture of films and molded products with low mechanical properties. Problems in the recycling of greenhouse films arise from the presence of products of photooxidation, which significantly affect the properties of a recycled material. An interesting possibility of use of photooxidized PE in blends with nylon-6 to improve blend compatibility has been demonstrated [13,14]. These follow from the earlier efforts [15,16] to compatibilize blends of polyamides and polyolefins (which are potentially very interesting, but, because of the strong incompatibility of both polymers, yield products having poor properties) with the use of functionalized polyolefins that can react with the amino groups of polyamides, giving rise to copolymers and thus stabilizing the blend.

Such functionalization, in general a long and extensive step, is mostly performed by chemical modification of the polyolefin structure. However, studies have demonstrated [13] that photooxidized PE offer similar results. Thus the use of recycled (photooxidized) greenhouse PE in blends with nylon give rise to PE/nylon graft copolymers during processing, which improve the mechanical properties of the resultant material. The graft copolymers act as compatibilizing agents; the properties of nylon-rich blends (80 wt% nylon-6) thus are found to be very similar to those of blends compatibilized by PE, and which is initially functionalized by chemical means. Moreover, in coextrusion, a good adhesion between the two layers (nylon and recycled PE) of coextruded films helps to avoid a need for the addition of a third layer binding two incompatible phases.

Chemical means such as glycolysis, methanolysis, and hydrolysis are good at unzipping only the condensation polymers—such as polyester, nylon, and polyurethanes—to facilitate chemical recycling.

Addition polymers, such as vinyls, acrylics, fluoroplastics, and polyolefins, can hardly be reprocessed except that, if they are sorted, they may be converted into powder by grinding operation and mixed with respective virgin resins for remolding into finished goods or, in some cases, blended with other resins using suitable compatibilizers to make useful end-products of commercial value.

Tertiary recycling of addition polymers require pyrolysis, which is a more aggressive approach. For mixed or unsorted plastics in particular, it is a practicable way of recycling. Pyrolysis is the thermal degradation of macromolecules in the presence of air. The process simultaneously generates oils and gases that are suited for chemical utilization.

The advantage of pyrolysis over combustion (quaternary recycling) is a reduction in the volume of product gases by a factor of 5–20, which leads to considerable savings in the gas conditioning equipment. Furthermore, the pollutants are concentrated in a coke-like residue matrix. It is possible to obtain hydrocarbon compounds as gas or oil.

The pyrolysis is complicated by the fact that plastics show poor thermal conductivity, while the degradation of macromolecules requires considerable amounts of energy. The pyrolysis of mixed plastic wastes and used tires has been studied in melting vessels, blast furnaces, autoclaves, tube reactors, rotary kilns, cooking chambers, and fluidized bed reactors [17,18].

Rotary-kiln processes are particularly numerous. They require relatively long residence times (20 min or more) of the solid wastes in the reactor. Moreover, due to the large temperature gradient inside the rotary kiln, the product spectrum is very diverse. For this reason, the gases and oils generated by the pyrolysis are normally used for the direct generation of energy and the process may well be considered as a quaternary recycling process.

For chemical recycling of mixed plastics, the fluidized bed pyrolysis has turned out to be particularly advantageous. The fluidized bed is characterized by an excellent heat and mass transfer as well as constant temperature throughout the reactor. This results in small dwell times (a few seconds to a 1.5 min maximum) [18] and largely uniform product spectra. The fluidized bed is generated by a flow of air or an inert gas (nitrogen) from below through a layer of fine-grained material, e.g., sand or carbon black. The flow rate is sufficient to create turbulent motion of particles within the bed. Using a fluidized bed pyrolysis, 25–45% of product gas with a high heating value and 30–50% of an oil rich in aromatics could be recovered [18]. The oil is comparable to that of a mixture of light benzene and bituminous coal tar. Up to 60% ethylene and propylene are produced by using mixed polyolefins as feedstock. Moreover, depending on the temperature and the kind of fluidizing gas (nitrogen, pyrolysis gas, and steam) different variants of the fluidized bed pyrolysis process can be carried out, yielding only monomers, BTX-aromatics, high boiling oil, or gas.

A promising concept that is receiving increasing attention is recycling plastics to refinery cokes, where pyrolysis units and a well-developed infrastructure are already in place. The main hindrance to the execution of this concept is the presence of contaminants (including chlorine and nitrogen) in the plastics stream, as well as the need to turn plastics into a liquid form that the refinery can handle. Projects are in place to address these issues. Initial small-scale pyrolysis, dissolving plastics into other refinery feedstocks, or turning solid wastes into a slurry, are some of the options that have received attention. Efforts have also been made in some refineries to convert mixed plastics into a petrochemical feedstock by catalytic hydrogenation. In the refinery, the aim of tertiary recycling is not to displace regular refinery capacity, but to use plastic waste as a very minor stream. However, even if all refineries with cokers took only 2% of their capacity as plastic waste, it would be extremely significant.

Mention should be made of a plastics liquefaction process that has been developed jointly by the Japanese Government Industrial Laboratory, Hokkaido, Mobil Oil Corporation, and Fuji Recycle Industry. The process can treat polyolefinic plastics (polyethylene, polypropylene, and polystyrene) or their mixtures by a combination of thermal and catalytic cracking to produce gasoline, kerosene, and gas oil fractions of about 85%. Recovered liquid and gas are separated by cooling and the gas is used as in-house fuel. The technology is unique in using proprietary Mobil ZSM-5 catalyst and has been described as an ultimate recycling technology [19].

A brief overview of several important aspects of plastics recycling and development in the field has been given above. Some of the topics that have been highlighted in this review will now be elaborated further in the following sections. In addition, waste recycling problems and possibilities relating to a number of common plastics will be discussed.

6.3 Recycling of Poly (Ethylene Terephthalate)

The largest use of poly (ethylene terephthalate) (PET) is in the fiber sector, with PET film and PET bottles representing only about 10% each of the total PET volume produced annually. A large percentage of the total PET output comprising films, plastics, and fibers is recycled by various methods and for several applications, which makes PET one of the largest in volume of recycled polymers in the world. Contributing to this is the suitability of PET for practically all recycling methods, which include direct reuse, reuse after modification, recovery of monomers and other low-molecular-weight intermediates, and incineration. Any particular method is selected on the basis of the quality of waste and scrap, the economy of the process, and the convenience of the operation.

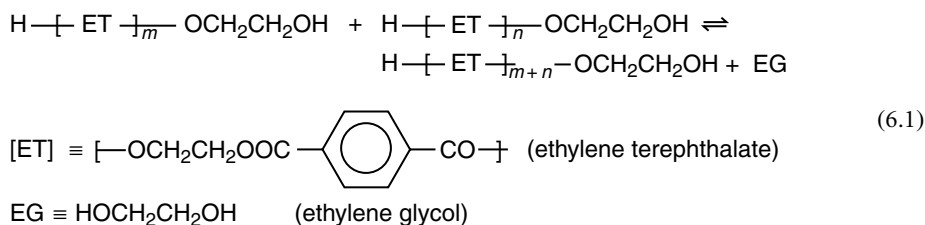
Contamination of post-consumer PET (POSTC-PET) is the major cause of deterioration of its physical and chemical properties during reprocessing. POSTC-PET is contaminated with many substances: (1) acid producing contaminants, such as poly(vinyl acetate) and PVC; (2) water; (3) coloring contaminants; (4) acetaldehyde; (5) other contaminants such as detergents, fuel, pesticides, etc., stored in PET bottles.

The most harmful acid to the POSTC-PET recycling process are acetic acid, which is produced by poly(vinyl acetate) closures degradation, and hydrochloric acid produced by the degradation of PVC. The acids act as catalysts for the chain scission reactions during POSTC-PET melt processing. Thus, the presence of PVC, as little as 100 ppm, would increase POSTC-PET chain scission [20]. Water reduces molecular weight (MW) during POSTC-PET recycling through hydrolysis reactions at the processing temperature (280°C). Moisture contaminants should be below 0.02% to avoid such MW reduction [21].

Acetaldehyde is present in PET and POSTC-PET, as it is a by-product of PET degradation reactions. The migration of acetaldehyde into food products from PET containers was a major concern in the early stages of developing the recycling process. Acetaldehyde being highly volatile, it can be minimized by processing under vacuum or by drying. Stabilizers such as 4-aminobenzoic acid, diphenylamine, and 4,5-dihydroxybenzoic acid are added to PET in order to minimize the generation of acetaldehyde [22].

6.3.1 Direct Reuse

This method, also called recycling by re-extrusion or melt recovery, is used for relatively pure PET waste such as cleaned consumer bottles or in-house waste. The method is based on the same principles as the original equilibrium polycondensation reaction:



As polymer buildup and polymer degradation are taking place in the melt simultaneously, the reaction conditions have to be controlled very carefully in order to obtain the desired molecular weight and molecular weight distribution for the end use. In theory, this seems rather simple; in practice, however, a large amount of determining parameters (temperature, environmental atmosphere, holding time in a melt state, amount of impurities, type of used catalysts, stabilizers, etc.) have to be kept under control.

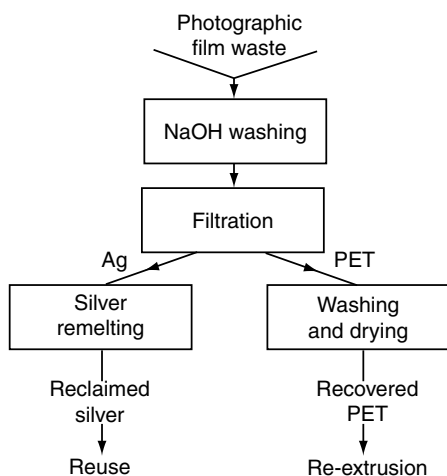


FIGURE 6.1 Combined recovery of silver and PET. (After De Winter, W., *Die Makromol. Chem., Macromol. Symp.*, 57, 253, 1992. With permission.)

various reclamation and reprocessing methods have been worked out and applied in practice. Because these processes are usually proprietary, the details of their operation are not known.

The larger use of PET film is as a photographic film base, which accounts for over 50% of the PET film produced in the world. The manufacturers of these materials, mainly Agfa-Gaevert, Eastman Kodak, du Pont de Nemours, Fuji, 3M, and Konishiroku, have long been interested in the recovery of PET film because of its content of rather expensive silver derivatives. Recycling of PET-film waste in production, which may amount to 25–30% of the total output, is almost complete by these manufacturers.

In a typical way of operation, PET film recycling is coupled with the simultaneous recovery of silver, as represented schematically in Figure 6.1. In the first step of the process, photographic emulsion layers containing silver are washed with, for example, NaOH, and after separation, silver is recovered on one side and cleaned PET waste on the other side [24]. Careful analysis is necessary to ensure that the washed PET-film scrap is clean enough to be recovered by direct extrusion.

The most obvious way of adding the recycled PET flakes is after the usually continuous polymerization and before the PET melt enters the extruder screw [25]. Such a procedure, however, has two main drawbacks: first, the highly viscous melt is difficult to filter (to eliminate possible gels or microgels); and second, other impurities (e.g., volatiles, oligomers, and colored parts) cannot be eliminated any more. In order to remove these disadvantages, several alternative modes have been worked out. A method to add recycled PET to the polymerization batch reactor during the esterification step was described by du Pont as early as 1960 [26]. Such a method shows the following advantages over the method described above: filtration can take place in the low-viscosity phase, and volatiles can be eliminated during the prepolymerization phase.

PET recycling by direct reuse, as described above, is by far the most economical process. However, it is useful in practice only for well-characterized PET wastes that have exactly known chemical composition (catalysts, stabilizers, and impurities). Therefore, the method is ideally suited for the recovery of in-production wastes, but it may not be suitable for post-consumer PET film.

6.3.2 Reuse after Modification

For post-consumer PET waste having a higher degree of contamination, technological processes based on degradation by either glycolysis, methanolysis, or hydrolysis can be used. These yield products that can be

A practicable reextrusion process was worked out and described by Syntex Chemie nearly forty 30 years ago [23]. This method—with some modifications—is still being used. The greatest recycler of fiber waste in the U.S. is Wellman; they recover PET fiber and bottle waste for home furnishing and nonwoven materials by a similar method.

Customer-recollected waste from fiber and textiles consists mainly of continuous filaments or staple fibers, which may be contaminated with dyestuffs, finishes and knitting oils, and other fibers such as cotton, wool, rayon, nylons, and acrylics; they are the most difficult-to-recover products.

A different picture can be presented for the PET bottles. In the environmentally active states in the U.S., 80–95% of the PET bottles sold are recollected and recycled. In Europe and in Japan where recycling has started earlier than in the U.S.,

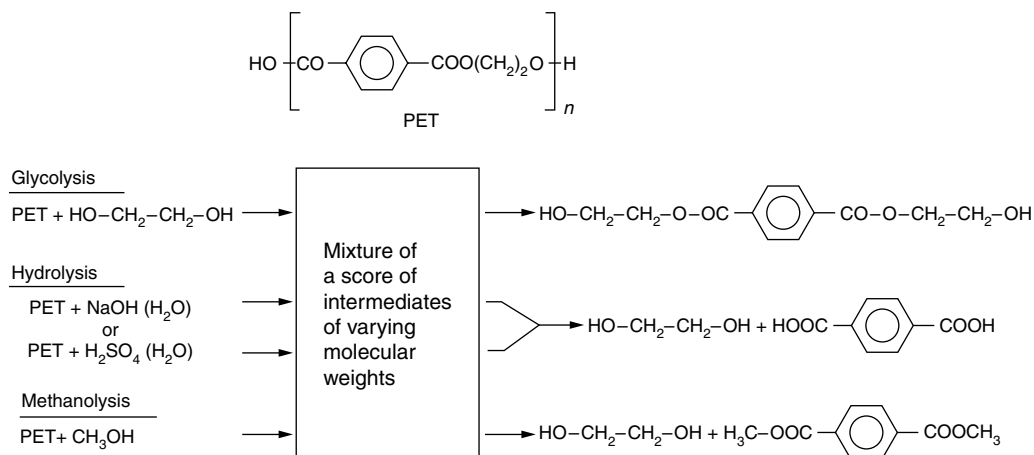


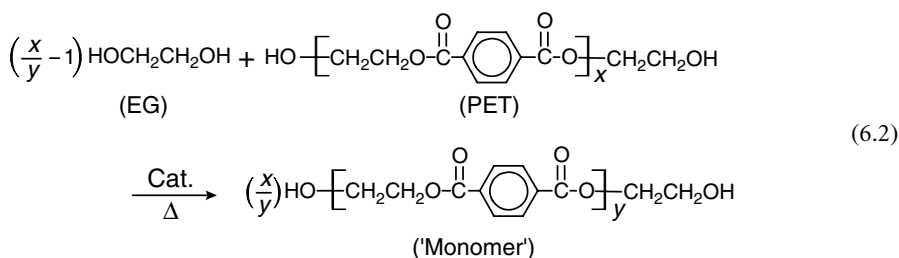
FIGURE 6.2 PET degradation by glycolysis, hydrolysis, and methanolysis. (After De Winter, W. 1992. *Die Makromol. Chem., Macromol. Symp.*, 57, 253.)

isolated. The principles of chemical processes involved in these methods are schematically represented in Figure 6.2.

Hydrolysis and methanolysis of PET regenerates the starting monomers. Thus, terephthalic acid (TPA) along with ethylene glycol (EG) are obtained by hydrolysis, while methanolysis yields EG and dimethyl terephthalate (DMT) among other products. Stopping short of complete depolymerization, glycolysis degrades long polymer chains (with typical repeat sequences of 150 units) into short-chain oligomers (repeat sequences of 2–10 units) having hydroethyl end groups.

6.3.2.1 Glycolysis

The addition of EG–PET reverses the polymerization reaction. This can be stoichiometrically represented by



where x = average number of repeat units in polymer and y = average number of repeat units in 'monomer.' When $y = 1$, monomer = dihydroxyethyl terephthalate (DHET).

Glycolysis thus represents a compromise between regeneration of starting ingredients by methanolysis or hydrolysis and direct melt recovery. It is less costly than the former and more versatile than the latter. The resultant, easily filtered, low viscosity 'monomer' can be repolymerized to a useful higher molecular weight product. A typical flow sheet of the process is shown in Figure 6.3.

PET scrap suitable for glycolytic recycle includes production waste, fibers, film, flake, and bottles. In a practical system, major contaminants are separated from feedstocks, e.g., bottle waste is cleaned and separated from a polyethylene base, paper labels, metallic caps, and liners. For many end uses, colored PET must also be segregated. (Highly modified copolymers, glass-reinforced resin, fiber, or fabric blends are not suitable for glycolysis. These can only be recovered by methanolysis/hydrolysis.) Since reaction time depends on surface area, PET feedstocks must be reduced to relatively small particles by grinding, cutting, etc.

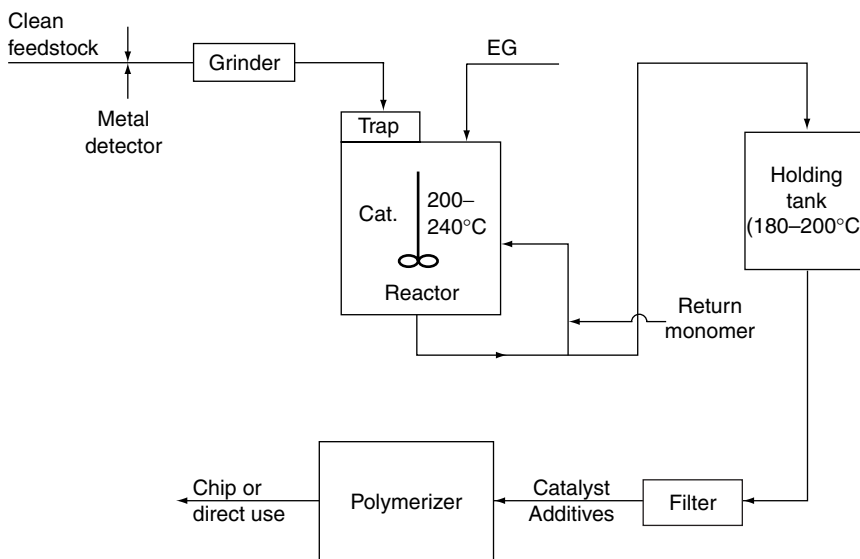
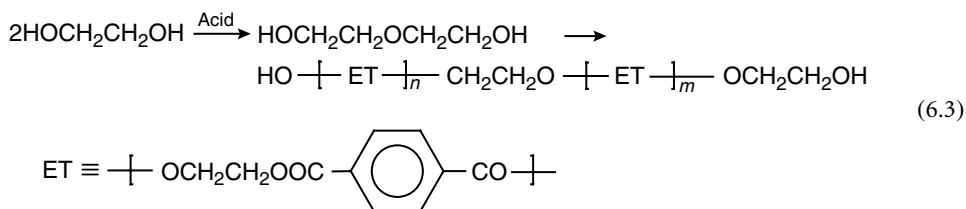


FIGURE 6.3 Flow diagram of a typical system for glycolytic recycling of PET waste. (After Richard, R., *ACS Polym. Prepr.*, 32(2), 144, 1991. With permission.)

The du Pont company [27] published many details covering the glycolytic recycling of PET. Goodyear has also developed a PET recycling process based on glycolysis that is called REPETE [28]. In a batch process, a molten 'monomer' heel is left in the reactor to allow the feedstock/glycol mixture to reach optimum reaction temperatures. In a continuous process (Figure 6.3) some of the molten 'monomer' is recycled to a stirred reactor to accomplish the same function. High glycol/terephthalate (G/T) ratios lead to more complete glycolysis but lower the maximum temperature, increasing the reaction time. A ratio of 1.7–2.0 G/T is a practical compromise [29]. An ester exchange catalyst as zinc or lithium acetate is usually added to increase the rate of glycolysis. Reaction temperatures of 220–240°C and times of 60–90 min are typical. The reactor is operated under a positive pressure to prevent forming an explosive mixture of air and glycol vapors.

The major side reaction is the production of ethers:



Since this reaction is acid catalyzed, it can be minimized by adding a buffer such as sodium acetate or by adding water [30]. Lithium acetate catalyst also produces less ethers than since acetate. Some other side reactions are the formation of aldehyde, cyclic trimer of ET, and dioxane. Oxidation of glycol ends produce aldehydes that lead to colored compounds. Traces of dioxane can form from the cyclization of glycol.

If other glycols, such as diethylene glycol, are substituted for ethylene glycol, the corresponding oligomers are formed. These can subsequently be polymerized with aliphatic diacids as adipic or 4,4'-diphenylmethane diisocyanate to give rigid elastomers [31]. Additive to control luster, color, and so on can be added in the usual manner before and after polymerization.

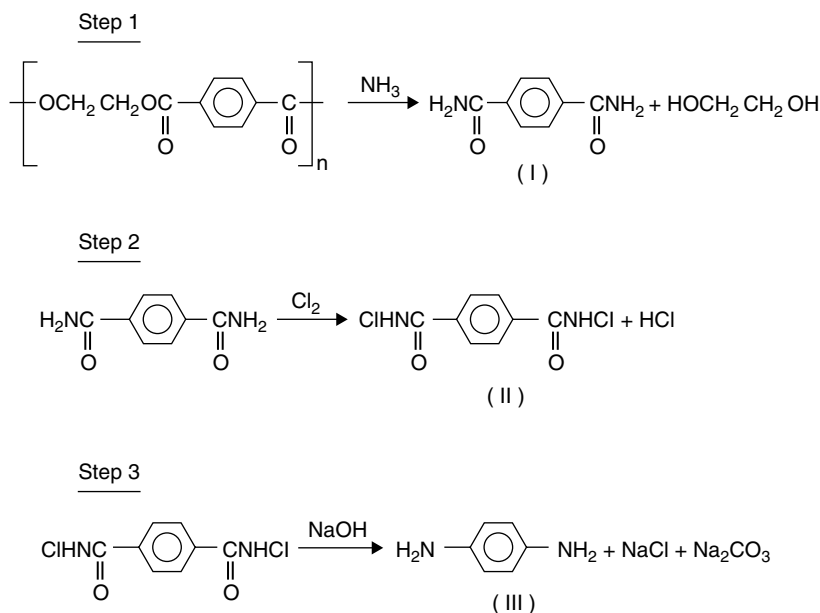
Primary uses for PET from glycolytic recycle are geotextiles, fibers for filling products, nonwovens, and molding resins where color, strength, and control of dyeability is not important. Recovered polymer can be added to virgin polymer for films, fibers, and molding resins.

6.3.2.2 Methanolysis

PET waste obtained in the form of film, bottles, and fibers can be very conveniently converted into its raw materials dimethyl terephthalate (DMT) and ethylene glycol (EG) by methanolysis. The process involves heating the PET waste with methanol at 240–250°C and 20–25 kg/cm² pressure in the presence of catalysts such as metal oxalates and tartrates. Once the reaction is completed, DMT is recrystallized from the EG-methanol molten liquor, and distilled to obtain polymerization-grade DMT. Also EG and methanol are purified by distillation. Eastman Kodak has been using such a process for recycling of x-ray films for nearly 40 years and it is still improving the process [32], e.g., by using superheated methanol vapor to allow the use of ever more impure PET waste. Important factors that have to be dealt with in this process are avoiding coloration due to aldehyde formation and minimizing the formation of either glycols.

6.3.2.3 Ammonolysis

PET wastes can be converted via ammonolysis to paraphenylenediamine, which is a basic raw material for the high-modulus-fiber Kevlar or for high-value hair dyes. The chemical basis for this process is a modified Hoffman rearrangement. The synthesis may be done via the following three stages [33]:



In the first step, granulated PET is suspended in ethylene glycol and treated with gaseous ammonia at 100–140°C. In this reaction, the ethylene glycol also acts as a catalyst. The product terephthalimide (I) is insoluble in the medium and thus may be isolated. In the second step, terephthalimide (I) is suspended in water and chlorinated vigorously with chlorine gas. The resulting terephthalic bis-chloramide (II) is treated with NaOH solution to obtain paraphenylene diamine (III). An important aspect of this process is that paraphenylenediamine so obtained is completely free from its ortho and meta isomers and its production cost is much less than the market price. ICI has reported an alternative single-step process for conversion of PET to paraphenylenediamine by ammonolysis in the presence of hydrogen gas.

6.3.2.4 Hydrolysis

PET can be completely hydrolyzed by water at higher temperatures and pressure in the presence of catalysts (acidic as well as alkaline) to regenerate the monomers, terephthalic acid, and ethylene glycol.

While both acid- and base-catalyzed systems are completely realistic, their usefulness under practical production conditions remain controversial. As far as acid hydrolysis is concerned, the large acid consumption and the rigorous requirements of corrosion resistance of the equipment make profitability questionable. Moreover, the simultaneous recovery of TPA and EG, requiring the use of ecologically undesirable halogenated solvents, is difficult and not economical. For the alkaline hydrolysis process, also, the profitability is strongly determined by the necessity of expensive filtration and precipitation steps. In spite of the fact that the majority of newer industrial PET-synthesis plants are based on the TPA process rather than on the DMT process [34], the hydrolytic method of PET recycling has not gained favor.

6.3.2.5 Depolymerization in Supercritical Fluids

The supercritical fluid over its critical point has high density, such as in liquid state, and high kinetic energy as in a gas molecule. Therefore the reaction rate is expected to be higher than the reaction under liquid state conditions. PET is depolymerized quickly by solvolysis in supercritical water [35] or supercritical methanol [36]. The main products of PET depolymerization in supercritical methanol are dimethyl terephthalate (DMT) and ethylene glycol (EG), as shown in Figure 6.4. The depolymerization is carried out typically at temperatures between 543 and 603 K under pressures of 0.1–15 MPa for a reaction time of 3–60 min. For example, at 573 K, sample/methanol ratio 1/5 (by wt) and reaction pressure 14.7 MPa, DMT yield is reported [37] to be 98 per cent in 30 min.

It has been suggested that random scission of polymer chain takes place predominantly in the heterogeneous phase during the initial stage of PET depolymerization in supercritical methanol producing oligomers, whereas specific (chain end) scission to monomers proceeds predominantly in the homogeneous phase during the final stage.

6.3.2.6 Enzymatic Depolymerization

In 1977, Tokiwa and Suzuki reported that some lipases, which are extracellular enzymes that usually cleave esters in oils and fats, are also able to attack ester bonds in some aliphatic polyesters and can depolymerize such materials [38]. Aliphatic polyesters, however, exhibit only limited useful properties for many applications. Aromatic polyesters, such as PET and PBT, which are widely applied because of their excellent properties, are not attacked by hydrolytic enzymes. This led to the development of aliphatic-aromatic polyesters as biodegradable plastics that present a compromise between biodegradability and material properties [39]. Recently, however, Müller et al. [40] have isolated a hydrolase (TfH) from *Thermofibida fusca* which is able to depolymerize the aromatic polyester PET at a high rate in contrast to other hydrolases such as lipases. They have demonstrated for the first time that commercial PET can be effectively hydrolyzed by an enzyme at a rate that does not exclude a biological recycling of PET. The effective depolymerization of PET with the enzyme TfH will result in water

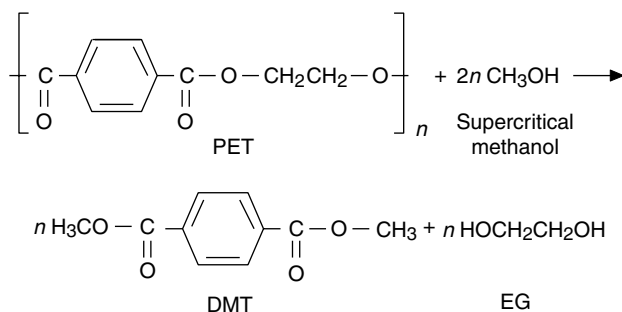


FIGURE 6.4 Main reaction of PET depolymerization in supercritical methanol.

soluble oligomers and/or monomers that can be reused for synthesis. In contrast, a microbial treatment of PET may not be appropriate for recycling purposes, since monomeric and oligomeric depolymerization products would be consumed by the microorganisms involved or inhibit their action and growth [40].

It is likely that the degradability of PET with hydrolases such as TfH strongly depends on the polymer crystallinity and the temperature at which the enzymatic degradation takes place [40]. The effective enzymatic PET hydrolysis will thus be expected to occur only below a certain critical degree of crystallinity. However, for bottle manufacture polyesters with low crystallinity are preferred for high transparency, thus increasing the susceptibility of PET to enzymatic attack.

One reason for the high activity of TfH hydrolase towards PET may be the high temperature (55°C) optimum, which is a result of its origin from a thermophilic microorganism. However, differences in the degradation behavior between TfH and the other lipases may also be due to differences in the structure of the enzymes, possibly enabling TfH to attack less mobile polyester segments and degrade PET at a surprisingly high rate.

6.3.3 Incineration

For PET wastes containing a large amount of impurities and other combustible solids it is more profitable to resort to quaternary recycling, that is, energy recovery by burning. Research along this line has been performed, particularly in Europe and Japan, since the early 1960s. Strong emphasis has been laid on the optimization of incinerators with regard to higher temperature of their operation and reduction of the level of air pollution.

Having a calorific value of ca. 30.2 MJ/kg, which is about equivalent to that of coal, PET is readily suited for the incineration process. However, like other plastics its combustion requires 3–5 times more oxygen than for conventional incineration, produces more soot, and develops excessive heat that thus calls for special incineration equipment to cope with these problems.

Several processes have been developed [41–43] to overcome the technological drawbacks of plastics incineration cited above. These include continuous rotary-kiln processes; a process for glass-reinforced PET; a combined system for wood fiber and PET to provide steam to power equipment; and a fluidized system for pyrolysis, in combination with silver recovery from photographic film. Incineration of photographic film raises the additional problem of the formation of toxic halogenated compounds due to the presence of silver halides.

Incineration of PET is usually carried out at temperatures around 700°C, since at lower temperatures waxy side products are formed, leading to clogging, while at higher temperatures the amount of the desirable fraction of mononuclear aromatics in the condensate decreases. A representative sample pyrolyzed under optimum conditions yields, in addition to carbon and water, aromatics like benzene and toluene, and a variety of carbon–hydrogen and carbon–oxygen gases. Studies have been made [44] relating to the formation of dioxines and residual ashes containing heavy metals and other stabilizers. While most problems arising during incineration of PET can be resolved, it is evident that quite a few hurdles remain to be overcome before an economically feasible and ecologically acceptable industrial technical process becomes available.

In conclusion, it may be said that there exists a clear hierarchy in PET-film recycling technologies. Two most important criteria of classification are the degree of purity of PET scrap to be handled and the economics of the process. While for the cleanest PET grade the most economical process is direct reuse in extrusion, for less-clean PET samples it is still possible to reuse them after the modification step (partial degradation, e.g., by glycolysis) at a reasonably low price. More-contaminated PET waste must be degraded into the starting monomers, which can be separated and repolymerized afterwards, of course, at a higher cost. For this operation, mostly the methanolysis process has been exploited industrially. Finally, the most heavily contaminated PET wastes have to be incinerated or brought to a landfill.

6.4 Recycling of Polyurethanes

Polyurethanes are by far the most versatile group of polymers, because the products range from soft thermoplastic elastomers to hard thermoset rigid forms (see Chapter 4). Although polyurethane rubbers are specialty products, polyurethane foams are well known and widely used materials. While the use of plastics in automobile has increased steadily over the years, a major part of these plastics is polyurethane (PU), which is used for car upholstery; front, rear, and side coverings; as also for spoiler. In fact, about half of the weight of plastics in modern cars is accounted for by PU foams. Accordingly, in addition to production scrap, large quantities of used PU articles are now generated from automotive sources. Though most PU plastics are cross-linked polymers, they cannot be regarded as ordinary thermosetting plastics, owing to their chemical structure and physical domain structure. Thus in contrast to typical thermosetting plastics, various methods are available today for recycling PU scrap and used products.

There are basically two methods for recycling polyurethane scrap and used parts, namely, material recycling (primary, secondary, and tertiary recycling) and energy recycling (quaternary recycling). The former methods are preferred since in this way material resources are replenished. After multiple uses the material can finally be used for energy recovery by high-temperature combustion or gasification.

Among several processes described for PU material recycling, thermopressing and kneader recycling [45] have attracted much attention. By the thermopressing process, granulated PU wastes can be converted into new molded parts, while in the kneader recycling process a thermomechanical operation causes partial chemical breakdown of PU polymer chains that can be subsequently cross-linked by reacting with polyisocyanates. Hydrolysis and glycolysis are important tertiary recycling processes for PU wastes.

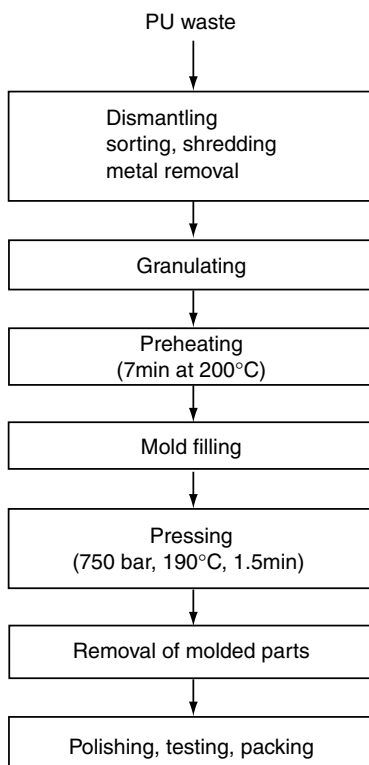


FIGURE 6.5 Reprocessing of polyurethane waste by thermopressing. (After Müller, P. and Reiss, R., *Die Makromol. Chem., Macromol. Symp.*, 57, 175, 1992. With permission.)

6.4.1 Thermopressing Process

Thermopressing, or molding by heat and compression, is a direct method of material recycling that is designed such that elastomeric, cross-linked polyurethanes can be recycled in much the same way as thermoplastic materials [46]. The principle of thermopressing is based on the realization that polyurethane and polyurea granules are capable of flowing into each other and building up new bonding forces under the influence of high temperature (185–195°C), high pressure (300–800 bar), and strong shearing forces. The granules generally used for this purpose have a diameter of 0.5–3 mm. They completely fill the cavities of a mold meaning that moldings with new geometries can also be manufactured.

Unlike injection molding of thermoplastics for which a cold mold is used, in the thermopressing process, the mold is kept constantly hot at a temperature of $190 \pm 5^\circ\text{C}$ and no release agent is used for demolding. This relatively simple technique will permit 100% recycling of polyurethane RIM and RRIM moldings, particularly when the formulations of RIM systems to be used in future have been optimized for recycling. The steps in the thermopressing process are shown in Figure 6.5.

The molded parts obtained by thermopressing of granulated PU waste exhibit only slight reduction in hardness and impact strength but significant reduction in elongation at break. The last named property, for example, drops to about 10% of the original value if painted PU wastes are used. Moreover, because of the use of granulated feed, the resulting molded parts lack surface smoothness and thus should be used preferably in those areas where they are not visible. In a passenger car, there are many such parts that are not subjected to tensile stress but require dimensional and heat stability—properties fulfilled by PU recycled products. Examples of application are wheelboxes, reserve wheel covers and similar other covers, mudguard linings, glove boxes, and casings.

6.4.2 Kneader Process

The basic of the kneader recycling process is a thermomechanical degradation of polymer chains to smaller-size segments. The hard elastic PU is thereby converted into a soft, plastic (unmolten) state, which is achieved with a kneader temperature of 150°C and additional frictional heating. This leads to temperatures above 200°C and causes thermal decomposition into a product that is soft at 150–200°C but becomes brittle at room temperature, enabling it to be crushed to powder in a cold kneader or roller press. The resulting powder can be easily mixed with a powder form polyisocyanate (e.g., Desmodur TT or 44 of Bayer) and molded into desired shapes by compression molding at 150°C and 200 bar pressure. The scheme of the recycling process is shown in Figure 6.6.

Partial breakdown of PU network in the kneader results in highly branched molecules with many functional groups necessitating addition of polyisocyanate in relatively high concentration for

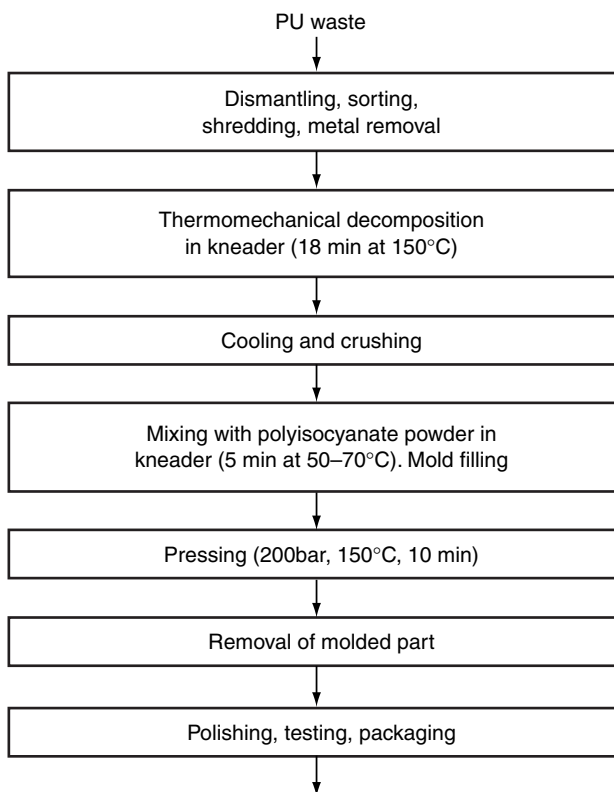


FIGURE 6.6 Recycling of polyurethane waste via partial decomposition in kneader. (After Müller, P. and Reiss, R., *Die Makromol. Chem., Macromol. Symp.*, 57, 175, 1992. With permission.)

subsequent cross-linking to produce molded articles. The process thus yields products of high hardness (with Shore up to 80) and high tensile strength (30 MPa), but small elongation at break (6–8%).

6.4.3 Hydrolysis

Hydrolysis of PU waste results in the formation of polyethers and polyamines that can be used as starting materials for producing foam. In this process, powdered PU waste is reacted with superheated steam at 160–190°C and the polymer gets converted in about 15 min to a liquid heavier than water. The liquid is a mixture of toluene diamine and propylene oxide (polyether diol), the former accounting for 65–85% of the theoretical yield:



The recovered polyether can be used in formulations for making PU foam, preferably in admixture with virgin polyether [47].

A continuous hydrolysis reactor utilizing a twin-screw extruder has been designed [47] that can be heated to a temperature of 300°C and has a provision for injection of water into the extruder at a point where the scrap is almost in the pulp state. Polyurethane scrap in powder form is fed into the extruder and residence time is adjusted to 5–30 min. Separation of the two components, polyether and diamine, in the product may be effected by fractional distillation, by extraction with a suitable solvent, or by chemical means. The PU foams made from these recycled products can be used in several applications, one example being protection boards for construction sites. Hydrolytic recycling has not, however, found much application, since virgin raw materials are cheaper than the regenerated products.

6.4.3.1 Glycolysis

Extensive studies have been made on glycolytic degradation of PU wastes. In a glycolytic process, powdered PU waste is suspended in a short-chain glycol and heated to a temperature of 185–210°C in nitrogen atmosphere. The glycolysis reaction takes place by way of transesterification of carbonate groups

in PU (Figure 6.7). The reaction product is predominantly a mixture of glycols and does not need any further separation of the components, unlike in the hydrolytic process. The cost of producing such recycled polyol is reported to be low enough to make the process economically viable [47].

The mixed polyols resulting from glycolytic degradation of PU waste is suitable mainly for the production of hard foam, such as insulating foam for houses.

6.4.3.2 Ammonolysis

Chemical recycling of polyurethanes by ammonolytic cleavage of urethane and urea bonds under supercritical conditions has been described [48]. It is well known that a number of low-boiling materials give enhance solubility and reactivity under supercritical conditions. Ammonia has a critical point at 132.45°C and 11.28 bar (11.28 MPa) with a density of 0.235 g/cm³. Being able to act as hydrogen-bond donor and acceptor, it provides good solubility for polyurethanes and

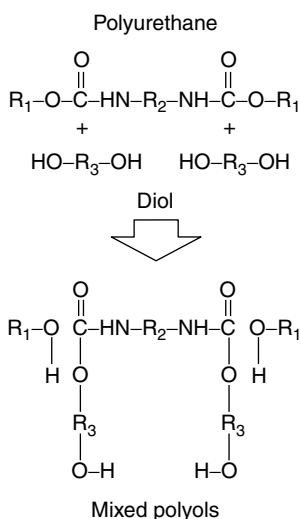


FIGURE 6.7 Alcoholysis of polyurethane (PU) waste. By the action of small-chain alcohols (e.g., diol), PU is decomposed yielding homogeneous, liquid, and mixed polyols.

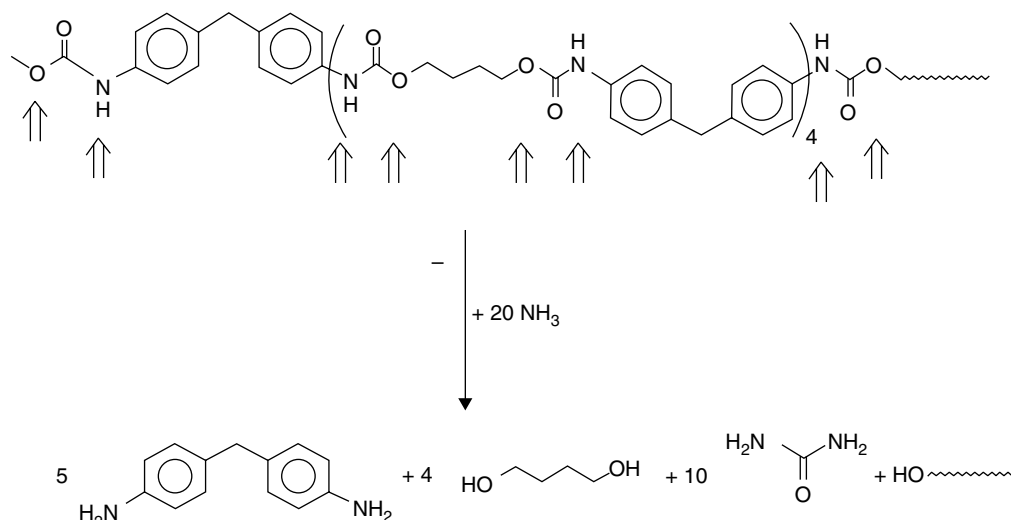


FIGURE 6.8 Stoichiometry of ammonolysis reaction of a polyetherurethane. (After Lentz, H. and Mormann, W. 1992. *Die Makromol. Chem., Macromol. Symp.*, 57, 305.)

dissolves their hard segment domains thus enabling a homogeneous reaction. Ammonia is also a reagent having greater nucleophilicity than, for example, water or glycol is; since it is added in a huge molar excess compared to the urethane or urea groups of the materials to be cleaved, the equilibrium is shifted towards the ammonolysis products. The stoichiometry of ammonolysis reaction of a polyetherurethane is shown in Figure 6.8.

The typical reaction parameters of an ammonolysis process are temperature of 139°C, pressure of 140 bar, and reaction time of 120 min. The ammonolysis reaction transforms derivatives of carbonic acid

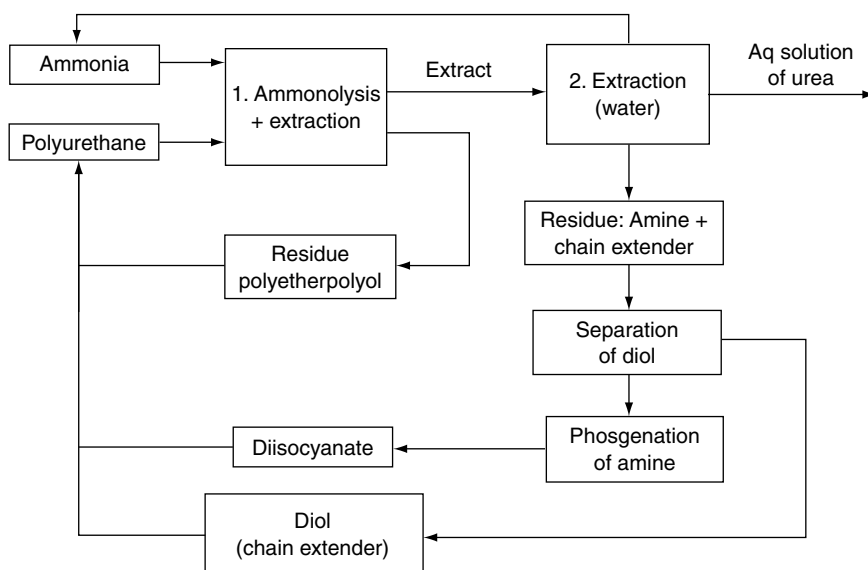


FIGURE 6.9 Flow scheme of a chemical recycling process based on ammonolytic cleavage and separation of polyol by supercritical ammonia. (After Lentz, H. and Mormann, W., *Die Makromol. Chem., Macromol. Symp.*, 57, 305, 1992. With permission.)

into urea. Ether bonds as well as hydroxy groups are inert towards ammonia under the reaction conditions applied. Hydroxy compounds like polyols and diol chain extenders that do not contain ester groups are recovered as such. The C=O fragments of urethane and urea functional groups are converted to unsubstituted urea.

After ammonolysis, ammonia is evaporated and can be reused after liquefaction, while degradation products of polyurethane hard segments (e.g., amines and chain extenders) and urea are removed by extraction. The pure polyol is left in the reactor. It can be removed mechanically or by extraction with liquid ammonia in which it is soluble. The recovered amines can be converted to the corresponding isocyanates and can be reused, along with polyols, in the same applications as before. A flow scheme of the recycling process is shown in [Figure 6.9](#).

Among the various material recycling methods for PU scrap and wastes described above, the thermopressing and kneading processes are especially significant, because these simple processes render the recycling of cross-linked PU products equivalent to that of thermoplastic products. Lack of surface smoothness and some reduction in mechanical properties are to be tolerated, especially when painted PU wastes are recycled. However, good values of E-modulus, structural rigidity, and hot and cold impact resistance permit use of the molded components of recycled PU in many applications, e.g., in unsighted parts of automobiles, instruments, and machineries.

6.5 Recycling of Poly (Vinyl Chloride)

Aside from the polyolefins, poly (vinyl chloride) (PVC) [49] and some other chlorine-containing polymers belong to the most widely applied thermo-plastic materials. There are many applications of rigid and plasticized PVC. In the building sector, for example, very large amounts are used for pipes, profiles for windows, floor coverings, roofing sheets and so on. By the end of the lifetime of these articles, large amounts of scrap have been produced. It is of economic and environmental interest to recycle this PVC waste as much as possible. Disposal of PVC waste by incineration has its special problems. Due to the high chlorine content of PVC, its incineration yields large amounts of HCl gas in addition to the possibility of formation of toxic dioxines and furans. On the other hand, it is a great advantage that many sources produce large amounts of PVC scrap of the same origin and with similar composition, which simplifies the reuse possibilities from a logistic point of view.

Dealing with post-consumer mixed PVC waste involves special considerations. Reprocessing PVC-containing plastics waste without separation will normally entail dealing with mixtures in which large proportions of polyolefins (mainly polyethylene) are present. In view of the poor compatibility of polyolefins with PVC, this is not a particularly attractive practical proposition, with respect to processing and the resulting product. Selective reclamation, i.e., separation from waste mixtures with other plastics, and subsequent reprocessing are complicated by the wide variety of PVC formulations, and the increased susceptibility to heat degradation in reprocessing. The main factors in the latter are the heat history already acquired; the possible presence of polymer already partly degraded in the course of past heat treatments and/or service; and the remaining stability of PVC articles before their recycling, which often necessitates an additional stabilization by addition of heat stabilizers. Moreover, about 1/3 of the used PVC is plasticized by various types of plasticizers. Therefore, for the recycling of such PVC types the concentration of plasticizers should be known. Due to these considerations, it is important to have rather detailed information about a PVC scrap before use.

6.5.1 Characterization of Used PVC

Since several chemical reactions occur during processing and use of PVC, which can change the properties of the polymer, it is necessary to characterize PVC scrap before deciding about the reusability.

Under the influence of heat and light (and also oxygen), PVC chains can be degraded or even cross-linked, which results in changes in the molecular weight and distribution and thus in the mechanical properties of PVC. For determining the molecular weight distribution, gel permeation chromatography

is the most applied method, but in many cases the measurement of solution viscosity after separation of all insoluble components, including cross-linked PVC, will suffice.

Because practically no PVC is processed and used without the addition of stabilizers, one should know the residual stability of a used PVC product. For this the best way may be the determination of the hydrogen chloride elimination at 180°C under air or nitrogen [50]. The conversion-time curves so obtained provide indication of the residual stability from the induction period and also enable calculation of the rate of HCl split-off after consumption of the stabilizers. In some cases, however, it may be sufficient to use a simple Congo Red test (e.g., according to DIN 53 418) instead of the apparatus for measuring the HCl elimination.

The dehydrochlorination of PVC results in the formation of polyene sequence that can be responsible for discoloration and also act as starting sites for further degradation and cross-linking reactions. For some applications it may thus be useful to have some knowledge about the unsaturated structures that have been formed in PVC during the use. For this purpose, the investigation of the UV-VIS spectra that give at least semiquantitative information about the dehydrochlorination and the application of ozonolysis [51], which results in cleavage of the unsaturated sequences in PVC, may be useful.

In the case of reuse of plasticized PVC, it is important to determine the residual plasticizer content. This can be obtained by extraction with ether or similar nonsolvents for PVC and determination of the chemical nature of the plasticizers by thin-layer or gas chromatographic methods. The determination of the glass transition temperature by differential thermal analysis also gives information on the efficiency of the residual plasticizers.

6.5.2 In-Line PVC Scrap

Normal recirculation, in the same process, of the clean PVC scrap generated (e.g., edge trim in calendering) is widely practiced, in particular with PVC for noncritical applications. General PVC scrap, both from internal and external sources, is also converted by some processors into such products as cheap garden hose or core composition for cables.

Two possibilities have been investigated for the recycling of die-cutting scrap produced in the processing of PVC sheet: production of secondary sheet and production of extruded profiles or pipes. First the scrap is ground up in a grinding mill. The stabilizer used in the original process is added again in a premixer, and pigments are often added to achieve a uniform, desired color. This premix is fed into the compounding unit.

If the regrind includes rigid, semirigid, and plasticized PVC, the rigid and semirigid fractions can be charged into the compounding unit through a first-inlet opening and plasticated in an initial kneading zone. The plasticized PVC scrap is then fed into this fluxed stock, which ensures the gentlest and most homogeneous processing (Figure 6.10). Any additional plasticizer required is injected directly into the

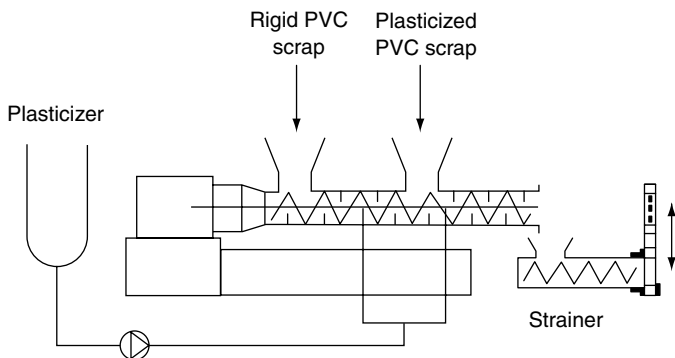


FIGURE 6.10 Recycling of PVC film scrap.

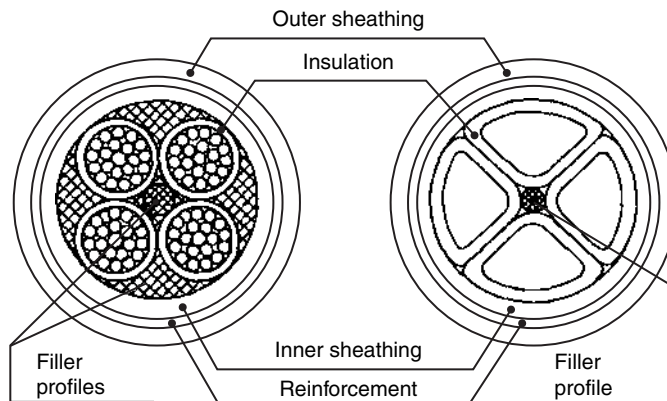


FIGURE 6.11 Schematic of cable design.

kneading zone of the compounding unit by a pump. This is done because the plasticizer cannot diffuse in the PVC regrind within a reasonable time, which it can in the case of virgin PVC. It is advisable to use a strainer in order to remove any contamination from the stock. Afterwards, the calendaring process is carried out as usual.

For the production of profiles and pipes, the homogeneous stock is pelletized following compounding. The pellets are fed to an extrusion line.

In the cable sector, compounders are often confronted with the problem of recycling copperless insulation and sheathing scrap. An approach that may be taken in this case is to use this scrap for producing filling core mixtures. The purpose of the filling cores is to fill out the cavities between a cable's conductors (Figure 6.11). Since their composition is not subject to any special electrical or mechanical specifications, it is normally made as inexpensive as possible, usually receiving a high level of chalk filler. The PVC in this case acts mainly as binder for the filler. For compounding such cable filler cores, the reground PVC scrap, with a particle size of 5–10 mm, is fed into the first inlet of a compounding unit designed specifically for this application (Figure 6.12). The reground scrap is plasticated homogeneously in the first kneader zone, enabling it to absorb the high filler loading fed into the second inlet opening without any difficulty. For increased flexibility of the filler cores, plasticizer may be injected into the kneading chamber by a pump (see Figure 6.12). The homogenized stock is pelletized following compounding.

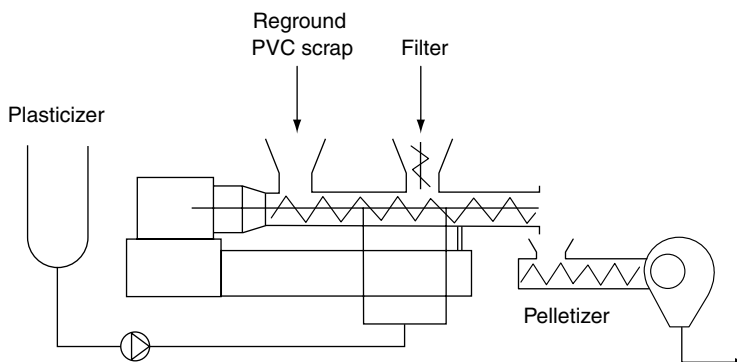


FIGURE 6.12 Compounding of cable filler cores.

6.5.3 PVC Floor Coverings

PVC floor coverings are a combination of a number of constituents that together comprise the recipe for a floor covering. Typical floor covering recipes are for the most part made up as follows: PVC 28–50%, plasticizer 10–20%, stabilizers 0.5–1%, slip agents less than 1%, filler 25–60%, and pigments 1–5%. Further, many floor coverings are provided with additional textile- or glass-fiber—containing carrier layers. Given an average service life of 10–17 years, old PVC coverings represent a large reserve of raw materials.

To exploit these large reserves of raw materials on an industrial scale, one needs a network for systematic collection of old coverings, a system of transport logistics, and the ability to build technically feasible recycling plants. In order to undertake this work in Europe, about 20 producers of PVC raw material and floor coverings from Germany and other European countries joined together in April 1990 to form the Society for the Recycling of PVC Floorings.

The main operations carried out in a recycling plant for old PVC floor coverings are sorting, cleaning, shredding, purifying, powdering, mixing, and packaging [52]. The purification unit essentially comprises a hammer mill and a downstream vibrating screen. The function of the hammer mill is to knock off any residues of screed or adhesive still adhering to the floor covering, and the vibrating screen then separates off these residues. The shredding material that has been purified in this way is first passed to a cutting mill, which enables it to be precomminuted to granules that are first homogenized in a mixing silo and purified by means of zigzag sifters before being processed to PVC floor covering powder in the powder mill. The powder can be upgraded by the addition of plasticizer, PVC, or filler to give powder recipes suitable for calendaring to make new floor coverings; this depends on the quality of the batch in question. Other possible uses of the powder are for products, such as mats for cars, mud flaps, and soft profiles.

6.5.4 PVC Roofing Sheets

A major use of PVC in the building industry is for roofing sheets. These sheets are produced on calenders and contain in most cases two plasticized PVC foils that are reinforced by glass fiber or polyester fabrics. The used sheets show different properties, depending on whether they are applied under direct influence of light and weather conditions and on the fact that in some cases these sheets on the roof are loaded with gravel or coarse sand.

After a lifetime of 10–20 years, the roofing sheets have to be replaced by new ones, which is normally done by the same firm(s). Therefore, the recycling of used roofing sheets is rather easy from the logistic point of view and has been common practice for many years. New PVC roofing sheets may contain up to 10% of the recycled material [52].

6.5.5 Post-Consumer PVC

Some post-consumer PVC sources are water, food, pharmaceutical, and cosmetic bottles, and film. Another significant source of post-consumer PVC is used electric cable, coming principally from plant demolition and, to a lesser degree, from manufacturing scrap and offcuts.

Most end-use markets for recycled plastic bottles require that they be separated by resin type and color. This ensures high end-use value for new products incorporating substantial amounts of the recycled resin. PVC bottles, like PET bottles, are very recyclable. Manual sorting of nonpigmented PVC and clear PET bottles is difficult because they look alike. When the two types are received commingled, the reprocessor can experience quality deficiencies due to rheological incompatibilities between these two resins. Therefore, all attempts to separate and remove these two resins must be made prior to recycling.

Manual sorting techniques are inadequate to meet the market's needed quality standards, so new techniques have been engineered that will detect and separate bottles made from either of these two resins. A simple device senses the presence of chlorine atoms as a means to detect PVC bottles.

Once detected, PVC bottles are pneumatically jettisoned from the commingled bottle feed-stream by a microprocessor-based air-blast system.

The step after sorting is baling or granulation. Granulation is the preferred method of intermediate processing since the material so processed commands the highest market value. For upgradation of the resin from the recycled PVC bottles, several steps are explored depending on the results of characterization tests as discussed earlier. These include incorporation of virgin resin (10–90%), restabilization against UV and heat, and incorporation of processing aids, impact modifiers, lubricants, plasticizers, and antioxidants.

The recovery of electric cable is long established because of its valuable copper content. After this conductor material has been extracted, the residue consists of sheathing and insulation that may contain rubber and polyethylene as well as PVC. These other materials can be largely removed from grinding, by flotation, vibration, and filtration, but rubber is especially difficult to remove entirely, so that applications for material recycled from cables containing it are limited to areas such as car mats and carpet underlay.

6.6 Recycling of Cured Epoxies

Thermosetting plastics are difficult to dispose because of their network structure. Chemical recycling is a promising route for converting these plastic wastes by returning them back to their original constituents. However, thermosetting resins are usually reinforced by reinforcement such as glass fiber to modify their brittleness and increase their strength, forming composite materials with complex structure. The presence of reinforcement in the cured composite thus makes the recycling of the matrix resin more difficult.

An approach to chemical recycling of amine cured epoxies using nitric acid solution has been proposed [53,54]. In order to investigate the practical applicability of the proposed research, glass fiber-reinforced bisphenol F type epoxy resin (cured with 4,4'-diaminodiphenylmethane) was decomposed in nitric acid solution and the decomposed organic products as well as the fiber were recovered. In a typical experiment, the glass-reinforced epoxy composite was cut into small pieces and kept immersed in 4 M nitric acid at 80°C till the matrix resin dissolved completely, yielding a yellow solution and leaving behind the inorganic (glass) residue which was separated and recovered. When the yellow solution was cooled in ice no crystal was formed. However, if nitric acid solution of higher concentration, such as 6 M, was used for immersion, crystals separated out because of breakage of the main chain of epoxy resin and subsequent nitration under the attack of nitric acid [55].

The yellow solution was subjected to neutralization with sodium carbonate, extraction, refinement, and drying to obtain neutralized extract (NE) which was then repolymerized to prepare the recycled resin. Since NE could contribute hydroxyl groups to bond with phthalic anhydride (curing agent), it was employed to substitute a part of epoxy resin. The proportions of NE addition ranged from 5 to 30 wt% (the ratio of weight of NE to the total weight of NE and epoxy resin). The process of neutralization and refinement of the acid extract is presented in [Figure 6.13](#).

6.7 Recycling of Mixed Plastics Waste

Commingled plastics currently represent an estimated two-thirds of today's recycled plastics streams. That fraction can be expected to shrink somewhat with the development of more successful identification and segregation technologies in the future. However, commingled plastics streams will continue to make up a significant volume for several reasons: proliferation of grades and types of commodity; profusion of polymer blends and alloys; contamination of recycle plastic parts with metals, coatings, and laminates; and practical cost considerations. Mixed plastics wastes can be divided into two groups depending on their source: mixed plastics from household or municipal solid wastes and plastics from industrial sectors.

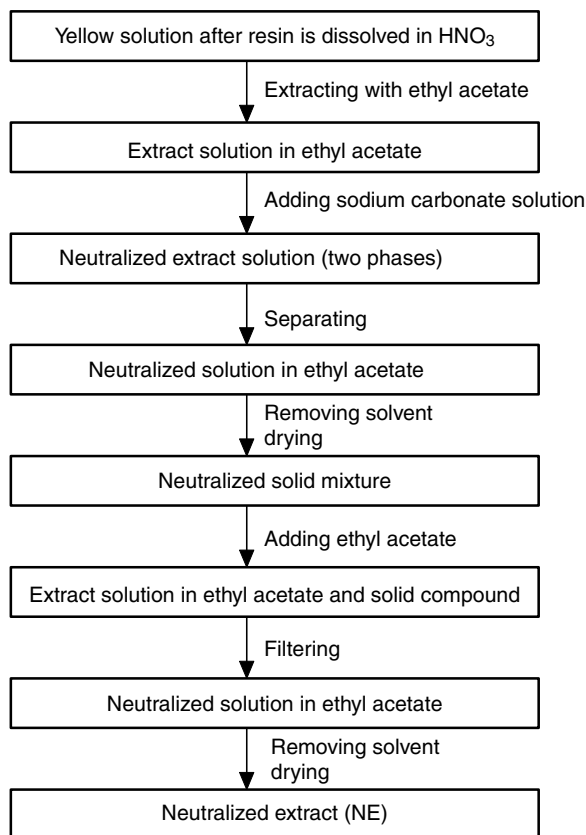


FIGURE 6.13 Process of extraction of epoxy resin dissolved in nitric acid and neutralization of the extract. (After Dang, W., Kubouchi, M., Sembokuya, H., and Tsuda, K., *Polymer*, 46, 1905, 2005. With permission.)

The first category (post-consumer mixed plastics) involves the articles that are used in food, pharmaceutical and detergent packaging, shopping, and others. The majority of these are composed of films, sheeting, strapping, thermoformed trays, as well as a variety of bottles for soft drinks, food, and cosmetics. There are mainly five different polymers—PE, PP, PS, PVC, and PET—that contribute to the total amount of plastics waste. The composition of mixed plastics can change depending on the regional habits and the seasons of the year. Also the mode of waste collection can influence its final composition.

The category of postindustrial wastes concerns articles like the products of the car, furniture, and appliances industries. The problems of these sectors is a wide variety of engineering materials and a high number of components employed to build a final system.

6.7.1 Direct Reuse

A direct solution to the problem of plastics disposal can be the reuse of a heterogeneous mixture of plastics directly obtained from an urban collection. Today there are extruders specifically designed for reprocessing post-consumer and postindustrial waste materials. The waste material can have many forms and can range in bulk density from approximately 1 to 35 lb/cu ft. The form, bulk density, moisture content, contamination level, and process-temperature restrictions all affect the design of the extruder to be used. For example, due to the presence of PVC resin, the melting temperature must be kept below 210°C and the barrel residence time must not exceed 6 min. Furthermore, in the mixture, the relatively high content of semicrystalline polymers like PET, whose melting point is above the processing

temperature, influences the extruder design or the final properties of the manufactured product. Large injection gates and mold channels must be used in order to avoid undesirable occlusions in the channels.

Standard single-screw extruders are no longer adequate to recycle or reclaim this wide range of materials in a cost-effective manner. There are now special extruders designed to process the lighter-bulk-density materials. Low-bulk-density materials are the various forms of film, fibers, and foams commonly used in the packaging industry. Due to their low-bulk density, such materials typically require an auxiliary device to facilitate proper feeding into the extruder throat. There are several varieties of such feeding mechanisms available [56]. Two of them are a rotating screw-type crammer and a piston-type ram. The crammer and ram systems both act on the same principle; that is, an auxiliary feeding device is used to convey and to compact the low-bulk-density materials into the feed section of the extruder screw.

The screw-crammer system uses a conical hopper with a screw that is driven by a separate gear reducer and variable-speed drive motor. The output and effectiveness of the crammer are determined by the screw configuration and the available speed. The ram-type system, on the other hand, uses a pneumatic ram to stuff material into the screw. The ram is a piston-driven unit with the stroke timing adjustable by setting a series of timers located in the control panel. The feed section used by the ram system has an opening that is 12–14 times larger than that of a standard screw extruder. This allows low-bulk-density material to flow freely into the feed throat where the ram can compress it into the screw. Depending on the extruder size, the ram can compact materials with a force of 2000–9000 psi.

Feed materials usually need to be supplied to either the crammer or the ram system in a chopped form. The size and bulk density of the chopped particles affect the performance of the crammer and ram, and thus ultimately the output of the extruder. Both these systems can also be used to process higher-bulk-density products.

A third method of processing low-bulk-density materials is through the use of a dual-diameter extruder [56]. This system has two distinct sections: a large diameter feed and a small diameter processing section. The large-diameter section acts as a cramming device—compacting, compressing, and conveying the feed material—while the smaller-diameter section is used to melt, devolatilize, and pump the extrudate into a die. In the feed section, the screw can have deep flights, allowing low-bulk-density materials to flow freely, while in the processing section the screw resembles that of a typical extruder. The screw is available in one of several configuration: single-stage, two-stage, or barrier design. Depending on process needs, these designs optimize output and raise product quality.

The feed section of a dual-diameter extruder can be equipped with feed-assist components that in some cases work in conjunction with specially designed screws to allow processing of a wide variety of feedstocks that are fed to the machines in roll form. Among these possible feedstocks are loose bags, handle cutouts from bag making operations, and continuous web products such as blown and cast film scrap. This ability eliminates the cost of shredding, grinding, and densification of many materials. A dual-diameter extruder is also capable of processing materials with a high-bulk density. The crammer, ram, and dual-diameter systems do not differ widely in equipment costs, or production rates.

It is well established that a strong incompatibility is typical of polymers usually found in commingled waste (PE, PP, PET, PVC, and PS). This incompatibility gives rise to materials that have inferior mechanical properties, particularly with regard to tensile, flexural, and impact strengths. This means a strong limitation of applications, in particular in the case of thin walls and manufactured products that have to work under flexural and tensile stresses. However, by adding to the mixture specific components like other polymers from homogeneous recycling, fillers (talc), fibers, or promoters (compatibilizers) that increase the compatibility, it is possible to improve the tenacity or stiffness, product aesthetics, and processability.

Addition of glass fibers, for example, is found [57] to yield products with very high stiffness (e.g., elastic modulus $E \approx 2800$ MPa with 30% glass fiber), higher than that with talc ($E \approx 1250$ MPa with 20% talc) and far better than that of the original mixture ($E \approx 950$ MPa). Addition of LDPE and styrene-butadiene-styrene copolymer, on the other hand, improves the tenacity (showing, typically, a 30–90%

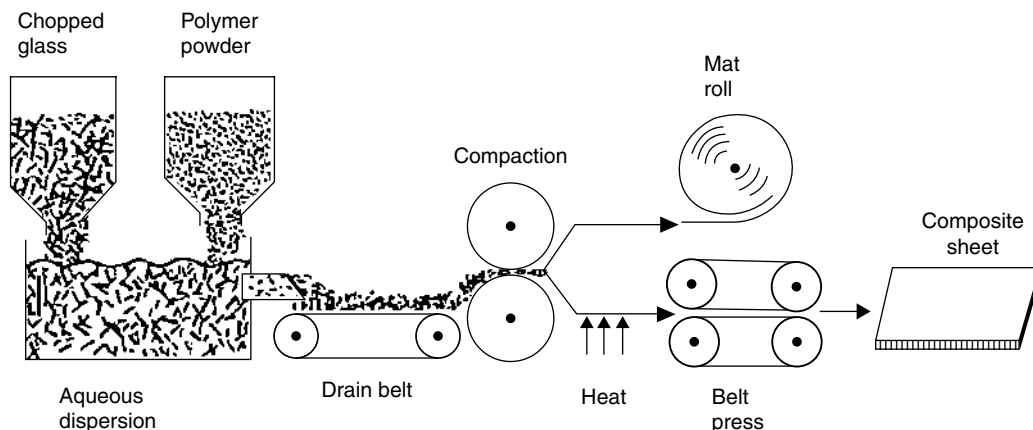


FIGURE 6.14 Schematic of Radlite technology.

increase in elongation at break). Extruded profiles have thus been made that can be employed to build benches, garden tables, bicycle racks, fences, and playing facilities for park. Coextrusion technology can be used very effectively to improve surface properties like puncture, impact and weather resistance, as well as appearance. One interesting application for mixed plastics, because of their large market volume, is the production of injected tiles for paving [57].

A new and exciting technology has been developed in the fabrication of composite materials made with commingled plastics. It followed the discovery in 1986 by the scientists and technologists at GE Plastics that useful products could be fabricated using Radlite technology (Figure 6.14) if the powdered feed consisted of two or more resins. While compatibilization of dissimilar resins is typically brought about by chemical means, this is not the case with Radlite technology products where compatibilization appears to take place by physical means, i.e., the binding of dissimilar resin domains through the fibers. A conceptual model of physical compatibilization is shown in Figure 6.15.

The rolls or sheets made by Radlite technology using commingled plastics and chopped glass fibers (0.25–1.0 in.) can be converted to finished parts by conventional forming technologies such as compression molding (typically 200–290°C, 3–5 MPa, 2–4 min). These are fully consolidated, essentially void-free products with specific gravities that would be calculated on the basis of resin type and glass fiber content. The physical properties of the consolidated structures from commingled plastics are in general similar to standard grades of SMC composites.

Foamed network structures (lofted structures) are also prepared in a compression press using Radlite technology. In this case, after applying full temperature and pressure for the requisite 2–4 min, the platen gap is opened 1.5 times the original setting (for primarily open-cell structure) or 1.1–1.2 times the

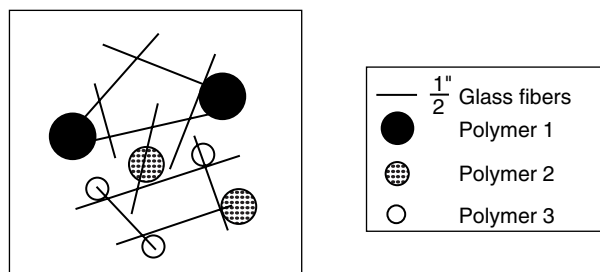


FIGURE 6.15 Conceptual model of physical compatibilization.

original setting (for primarily closed-cell structure). Foamed structures have the aesthetic and physical appearance of particle board, a common material of construction. Application possibilities of products made by the Radlite technology include highway signs and sound barriers, substructures for bathtubs and shower stalls, pallets and tote boxes, and flooring products and building fascias.

A novel application of mixed plastics is to toughen road surfaces. In 1986, the Ragusa Laboratories of ECP Enichem Polimeri in Italy investigated the use of mixed plastics waste to reinforce bitumen. Sorted municipal waste with a polyethylene content of approximately 60% was mixed with bitumen in varying proportions up to 20%. The properties of the resultant bituminous concrete were improved in two important ways: better wear resistance and raised softening point. Use of bitumen modified with mixed plastics waste of high polyethylene content as an experimental road surface under heavy traffic has established its notable superiority over unmodified bitumen for road surfacing.

6.7.2 Homogeneous Fractions

A widespread solution, in terms of application and market volume, could be the recycling of single materials or homogeneous fractions obtained from a separation process of the mixture. In fact, the samples obtained from single homogeneous fractions show a general performance far greater than that of samples produced from mixed plastics. Separation of post-consumer mixed plastics (municipal waste) into four fractions—polyolefins (PO), PS, PVC, and PET—is commonly adequate.

The improvement of tenacity is, in particular, evident when considering impact resistance of PO as compared to mixed plastics. Samples subjected to impact tests show an increase in elongation at the breaking point from 7% to above 100% [58]. The samples of recycled PVC fraction are comparable with those of a common virgin, with only marginal reduction in mechanical properties.

With regard to PET fraction, the potential applications are strongly dependent on its purity (as discussed earlier). Applications like films, fibers, or straps are not recommended when a high concentration of impurities are present. In this case, the PET fraction can be employed for structural applications as an engineering polymer with the addition of other components like glass fibers, impact modifiers, and/or nucleating systems. However, reuse of the PET fraction implies that the amount of residual PVC must be kept below 50 ppm to avoid undesirable polymer degradation that results in poor surface appearance and loss of mechanical properties of the manufactured products.

Mixed waste consisting of PET and PE can be converted into useful products using compatibilizers such as LDPE and LLDPE with acid and anhydride groups grafted on the backbone. A range of products can be made with such compatibilized blend, e.g., office partitions, roofing, slates for benches and chairs, and generally any extruded or molded sections needing mechanical load-bearing capacity similar to aforesaid applications.

With advances in cleaning, sorting, and other recycling technologies, more products with recycled plastics content are being manufactured. Some recent developments include using recycled PP and HDPE to produce a wide range of products. For example, multimaterial PP bottle scrap (typically, 90% PP, 5% ethylene-vinyl alcohol barrier resin, and 5% olefin adhesive) can be added in varying amount (3–12%) to recycled HDPE and processed on a single-screw extruder to form pellets for compression molding to a range of products. The multimaterial resin can also be sandwiched between two layers of virgin HDPE using a three-layer extrusion blow-molding process. Bottles made in this way from 75% virgin resin and 25% post-consumer blend are found to be suitable for normal commercial trade [59].

6.7.3 Liquefaction of Mixed Plastics

There have been many research activities on plastics liquefaction because oil is easy to store, transport, and use. Most promising among them is the liquefaction technology jointly developed by the Japanese Government Industrial Development Laboratory (Hokkaido), Mobil Oil Corporation, and Fuji Recycle [60]. The process features a combination of thermal and catalytic cracking using a proprietary Mobil

ZSM-5 catalyst. It can treat polyolefinic plastics, PE, PP, PS, or their mixtures, producing relatively low pour and highly aromatic liquid at a yield of about 85%. The produced oil contains many aromatics including benzene, toluene, and xylene.

Waste plastics are crushed, washed, and separated from other plastics that cannot be liquefied (e.g., PVC) by utilizing the difference of specific gravities against water. Plastics that can be liquefied mostly float in water while plastics that contain a lot of chlorine, carbon, and oxygen have high specific gravities and sink in water. However, some PVC floats and is recovered with PE or PP. Therefore, after separating, the feedstock for liquefaction may still contain 3–7% PVC. Fuji Recycle has developed liquefaction technology to treat such PVC contaminated mixtures [60].

For liquefaction, polyolefinic plastics are warmed to about 250°C, melted and transferred to the melting vessel by a heated extruder. In the melting vessel, plastics are further heated to about 300°C by heat transfer oil and transferred to the thermal cracking vessel. In the thermal cracking vessel, melted plastics are heated to about 400°C by the cracking furnace. The thermally cracked gas phase hydrocarbon passes through the catalytic reactor containing ZSM-5, where it is cracked and converted to higher-value hydrocarbon. The recovered liquid and gas are separated by cooling and the gas is used as in-house fuel.

Because of the pore structure of ZSM-5, the produced hydrocarbons are composed of low molecular species (4 carbons to about 20) which are in the gasoline, kerosene, and gas oil boiling range. In comparison, the carbon numbers of hydrocarbons produced only by thermal cracking range from 4 to 44. Polystyrene in the feedstock enhances the yield of ethylbenzene, toluene, and benzene, while producing gas that is predominantly propane/propylene.

6.8 Post-Consumer Polyethylene Films

Driven by consumer and legislative pressures, post-consumer film recycling has gained momentum and is now one of the fastest-growing segments of the recycling industry. post-consumer films consisting of LDPE, LLDPE, and HDPE, which are accounted for mostly by grocery sacks, stretch and shrink wrap, agricultural film, packaging, and blow-molding drums, and have thicknesses ranging from 0.2 to 5.0 mils. Film recycling was first developed in Europe for agricultural film, which is relatively easy to process due to its high-bulk density and minimal contamination. Today, interest in recycling systems for film of varying thickness and resin types has changed the design of a recycling line to one that uses both high and low-bulk-density material.

The primary challenge to recycling film is contamination. According to an industry estimate, up to 25% of all grocery bags are contaminated and require very thorough washing in the recycling process. A typical route for recycling plastic bags is shown in Figure 6.16.

Bales weighing 600–800 lb, collected by commercial haulers, film-generating business, or the solid-wastes-handling industry, are first fed into a breaker-shredder. The shredded material then passes over a vibratory conveyor or through metal-detection systems to remove ferrous and nonferrous contaminants. Film is next sent to a sedimentation tank for removal of rocks or dirt before going into the granulator

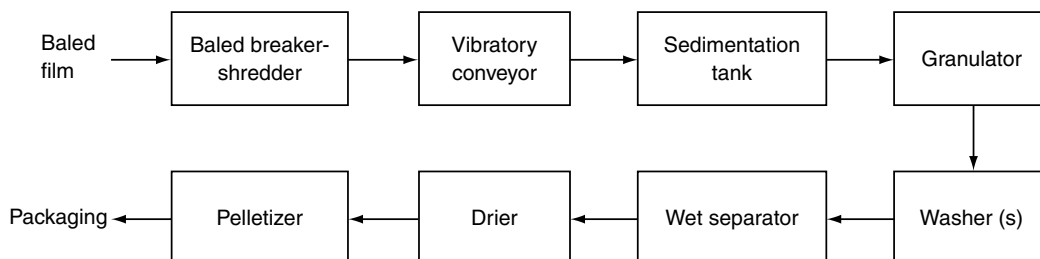


FIGURE 6.16 Typical route for recycling plastic bags.

(usually wet) for size reduction. Granulated into flake, the material then passes to a hot wash for removal of glue, residues, and remaining labels. Depending on the feedstock and the extent of contamination, the film may go through more than one wash cycle.

After the wash, the material moves to the separation stage. Two most common methods for separating plastics by resin type are float-sink and hydrocyclone. The float-sink method is less costly but requires a relatively large tank size in order to realize volume effectiveness. A hydrocyclone is more costly, but uses less water, has no moving parts, and generally takes up less space than the older float-sink method.

The flaked material from the wet separator, described above, goes through a drying and dewatering stage to an extruder, where in the melt phase the plastics can be mixed with dyes and other product enhancements, and then filtered and forced through a die for fabrication of free-flowing pellets. Depending on the mixture of LLDPE, LDPE, and HDPE, the pellet can be tailored for specific markets. Low-quality pellets are often sold as a commodity in the general marketplace. High-quality blends of polyethylene are suitable for many nonfood film applications.

One major market for recycling film is packaging. Many consumer-products companies have already turned to detergent bottles and other packaging made with significant percentages of recycled HDPE. Another fast-growing outlet is coextruded blown film used in trash bags, in which post-consumer resin is sandwiched between virgin layers of high-molecular-weight HDPE. The coextrusion technology allows high percentages of reprocessed material to be incorporated into virgin resin.

In many countries, legislation is a key driving force behind greater recycling efforts. Several states in the U.S. have passed recycling content standards mandating that virgin plastics used in some applications, such as grocery and trash bags, contain a certain percentage of recycled material. In California, for example, trash bags are required to have 30% recycled post-consumer content. Germany requires that 64% of all packaging materials be recycled. Under the German system, all types of plastics packaging are collected together and subsequently segregated into several categories: rigid containers; films; cups, trays, and blister packaging; and foamed material. The materials are then offered back to industry for recycling purposes at no charge.

6.9 Recycling of Ground Rubber Tires

Discarded tires represent a significant component of the overall plastics recycling challenge. They are an easily segregated, large volume part of the waste stream and present their own, somewhat unique, waste recycling problems. Some of the methods of utilizing scrap tires that have been investigated [61–63] are: burning, pyrolysis, use in cleaning up oil spills, road surfaces, roofing materials, and playground surfaces. While some of these approaches have been put into practice, the scrap tire disposal problem is clearly a case where supply far exceeds available use, pointing to the need for new methods of utilization and/or technological advances to extend the existing ones.

One area that has the potential to utilize large volumes of discarded tires is the need for a filler in polymer composites. Although the use of ground rubber tire (GRT) as a filler in polymer blends is a potentially attractive approach, it is fraught with a number of difficulties. Generally, when the large GRT particles are added to either thermoplastic or thermoset matrices, there is a large drop in mechanical properties, even at relatively low filler loadings [64]. Since the approach here is to use the GRT as a low-cost additive, and as there are a number of other materials competing in this regard, overcoming this large drop in properties has to be accomplished with little added cost (both in terms of additives and additional processing). This has proven to be quite a challenging task.

In order to be used as a filler in polymer composites, tires are first ground into a fine powder on the order of 100–400 μm , which is accomplished typically through either cryogenic or ambient grinding. The large rubber particle size used in GRT composites is reported to be one of the two major factors (the other being adhesion) contributing to the poor mechanical properties generally observed for GRT-polymer composites. In general, a low particle size is desired for optimum composite properties.

In GRT-polymer composites, however, the particle size is quite large. Since there is very little breakdown of the particles under normal melt blending conditions due to the highly cross-linked nature of GRT, the particle size is to be controlled only by the grinding process, which in turn, is influenced by process choice and economics.

In order for GRT to be used as an economical filler, the particle size has to be kept as large as possible to minimize grinding costs. Typically, the lower limit on particle size necessary to produce economical composites lies in the 40–80 mesh ($\approx 400 - 100 \mu\text{m}$) range, while for rubber toughening applications it is generally reported [65] that the optimum particle size for toughening brittle polymers is in the 0.1–5 μm range. Thus the size gap is large. Though it adds to the cost, there may be some advantage in going to smaller particle sizes if significant gains in mechanical properties are realized. The detrimental effects of adding GRT to cured rubbers decreases as the particle size is decreased [66]. For GRT recycled back into tires, for example, the detrimental effects are almost eliminated [66] with the use of ultrafine (20 μm) rubber.

As mentioned above, simple addition of GRT to most polymers results, in general, in significant decreases in mechanical properties due to large particle size and poor adhesion. Although some of these materials may find limited application in low-level usages, there is clearly a need to improve on the properties of GRT-polymer composites for them to become a large-volume material. Since lowering particle size to effect any substantial improvement in material properties adds significantly to grinding costs, strategies for overcoming the deleterious effects of adding GRT to polymers have focused on methods of improving adhesion.

The poor adhesion is, at least in part, due to a high degree of cross-linking in the GRT particles. The highly cross-linked nature of the particles inhibits molecular diffusion across the interface so that there is little or no interpenetration of the phases, resulting in a sharp interface. There have been a number of reports of processes that claim to improve properties of GRT-polymer composites through enhancing adhesion. The use of an aqueous slurry process using a water-soluble initiator system to graft styrene to GRT has been reported [67]. The styrene-grafted GRT particles are found to give composites with properties superior to straight mechanical blends.

Precoating of GRT particles with ethylene/acrylic acid (EAA) copolymer is found to improve the mechanical property, which is attributed to an interaction (H bonding) between the EAA copolymer and functional groups on the GRT surface, resulting in increased adhesion [68]. Thus a blend of 40 wt% EAA coated GRT particles (4 wt% EAA) with LLDPE was shown to have impact and tensile strengths 90% of those for pure LLDPE, representing increases of 60% and 20%, respectively, over blends with uncoated particles. The use of maleic anhydride grafted PE (PE-g-MA) resulted in increases in the impact strength of LLDPE-GRT composites of as much as 43%, without the need for a precoating step [68].

Electronic spectra for chemical analysis (ESCA) of GRT surface reveal an oxygen surface content of 5–15%, which may indicate the presence of $-\text{OH}$ or $-\text{COOH}$ functionalities. Since the epoxy group readily reacts with a wide range of functional groups such as $-\text{OH}$, $-\text{COOH}$, $-\text{SH}$, $-\text{NH}_2$, the use of ethylene-co-glycidyl methacrylate (EGM) as a coupling agent [68] has been investigated. A significant increase in impact behavior has been observed. It is seen that judicious selection of a compatibilizing agent can lead to composites with quite reasonable mechanical properties at significant levels of GRT (as high as 50–60 wt%). Because added compatibilizer levels are low (4–7 wt%) and no specialized processing steps are necessary, these higher-value composites can be produced at little additional cost over simple GRT-polymer blends.

It has been observed recently [69] that special treatment of GTR by bitumen confers outstanding mechanical properties on thermoplastic elastomers (TPEs) produced using the treated GTR. Typically the reclamation of GTR by bitumen is carried out by preheating the GTR/bitumen blend (1/1 by weight) at 170°C for 4 h in an oven, followed by rolling on mill rolls at about 60°C for 40 min. Thus, high performance TPEs, based on recycled high-density polyethylene, ethylene-propylene-diene monomer (EPDM) rubber, and GTR treated with bitumen has been prepared. It has been concluded that bitumen acts as an effective devulcanizing agent in the GTR treatment stage. In the subsequent steps of TPE

production, bitumen acts simultaneously as a curing agent for the rubber components (EPDM/GTR) and as compatibilizer for the blend components.

6.10 Recycling of Car Batteries

Polypropylene (PP) is obtained in segregated form as casing fragments from reprocessing of used lead-acid batteries from automotive applications. Because the casing makes up about 7% of the total battery and the used batteries are recycled primarily for lead recovery, PP is obtained without additional cost and in substantial quantities to warrant the operation of a plastics recycling plant.

In the first step of a typical recycling operation, the batteries are processed through a crushing and separation system operating on the TONOLLI principle (Figure 6.17), which has been successfully employed in various battery recycling plants in Europe and North America. The heavy fraction (lead, lattice metal) and ebonite are then separated from the light fraction (PP and impurities). The PP at this stage has a purity of 97%, which is still insufficient for its further processing. It is therefore sent to an upgrading stage, where it is further reduced in size in a wet-type rotary grinder and subsequently separated from water by sedimentation. After passing through two series-connected driers and a cyclone separator, the PP is available as so-called regrind with a purity of 99.5%. As the regrind consists of various types of PP differing in their formulation, molecular composition, and stabilizer content, it has a broad spectrum of characteristics. Suitable mixing can be done to obtain an intermediate product with a narrowed range of statistically uniform product characteristics.

In the next step, the regrind is routed to a compounding plant where—with controlled addition of additives, polymers, and fillers—the feed mix can be adjusted to suit the specific customer requirements. This feed mix is then metered into a special twin-screw kneader where it melts under the dual action of an external heater and internal shear forces, producing a homogeneous compound. Volatile matter is vented and unmolten impurities are filtered out. The melt is subsequently palletized in a melt granulator and the resulting granulate is quenched in a water bath, centrifuged, and finally passed through a hammer mill to break up lumps. The end product is a granular secondary raw material and suitable for injection molding.

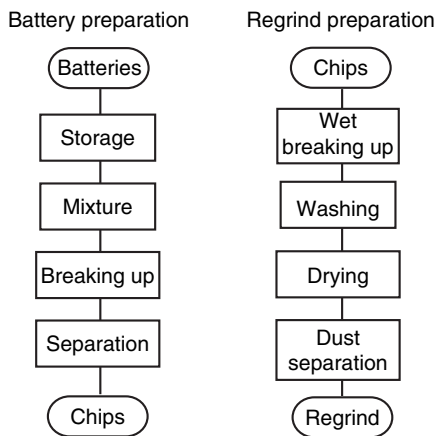


FIGURE 6.17 Process steps in preparation of polypropylene regrind.

6.11 Plastic Recycling Equipment and Machinery

While the plastics recycling activity, driven by consumer and legislative pressures, is all but certain to increase, the key variables in the rate of growth are the plastics industry's ability to develop an economical material-collection infrastructure and to improve the methods for handling and processing of contaminated scrap. Techniques for selection and recycling of post-consumer plastics are, however, closely related to the characteristics of plastics containers consumption, which vary greatly according to the geographical areas and the relevant law regulations governing activities in this sector.

Consumption features play a major role in the choice of the materials to be recycled. In the United States and Canada, the materials chiefly recycled are PET bottles and PE containers; in France, on the contrary, recycling of PVC got priority on account of the large quantity of such material used in the

packaging of drinks. In Australia, recycling includes primarily PET and PE, whereas in Japan it is mainly PET. In Italy, the plastics recycled are mostly PET, PVC, and PE. In short, the material to be recycled and the enforced legislation determine the choice of collection system. In many countries such as United States, Canada, Australia, France, Austria, and Switzerland, some fractions of post-consumer plastics are collected in the most homogeneous way possible. In other countries, plastics are collected more heterogeneously, that is, different types of plastics out of different types of manufactured articles, such as foil, containers, bottles, are collected together.

The outcome of the collection system constitutes the raw material for the recycling process. The degree of purity of this raw material evidently depends on how selective the collection is.

6.11.1 Plastocompactor

For voluminous scraps such as light film, textiles, fleece, and foam, it is advantageous to increase the density, which may be in the range of 20–40 kg/m³, to about 400 kg/m³ for transport reasons and for further processing. With thermoplastics and thermoplastic mixtures, a *plastocompactor* can be used for this purpose. It is, however, more useful for homogeneous fractions of thermoplastics. The process agglomerates the material without plastifying it. By heating the material locally for a short period to a temperature above the softening point, the soft components begin to adhere. The material is then compacted into a condition very similar to the virgin material.

In a typical agglomeration plant, the loose material is usually fed to a granulator, which is also fitted with a nip roll device for feeding continuous material such as fleece or film from the roll. A blower transports the flakes from the granulator to a holding silo. The discharge screw in the silo transports the flakes to the feed hopper from where they are carried by a blower to the plastocompactor. A dosing and pressing screw feeds the actual agglomerator part of the machine. This comprises essentially two discs—one rotating and the other stationary—between which the flakes are compacted by using heat from friction and pressure. The agglomerate leaves the discs through the outer gap in the form of warm soft sausages and is cooled immediately by an air stream. It is then fed, in a semisoft state, to a hot melt granulator where it is reduced to a free-flowing granulate.

6.11.2 Debaling and Initial Size Reduction

The first operation of the recycling process is the cleaning of foreign bodies. It requires a number of operating steps, the first being normally a debaling operation as the collected material, for transport reasons, is reduced into bales. Debaling is still often carried out manually. The reason often given for using a manual method is that the workman can also check the baled scrap for large pieces of foreign matter at the same time. However, there exist very efficient debalers for making the task automatic, and the best brands are equipped with specific devices designed in accordance to the composition of the bales to be loosened. Such factors as the forms of plastics items; the proportion of PE, PET, or PVC in the bales; the collection features; the container typology; and the share of foil plastics determine the type of debaler construction technique.

Two simple debaling services are a grab truck and a screw shredder. A grab truck can normally be used for bales of film. Sitting in his machine, the workman can break open the bales using three hydraulically operated grabs fitted to an extension arm. Checks for large pieces of foreign material can also be conducted. Using the same grabs, the loosened material can then be placed onto the feed conveyor fitted with a metal detector.

For bales containing individual items of scrap such as bottles and other hollow items, the use of a screw shredder offers many advantages. This machine is fitted with a very large feed hopper and can be fed directly with a large bucket loader or similar device. The feed material is reduced by a tearing process in the shredder between independently driven screw shafts fitted with shredding teeth. Screw shredders are manufactured with up to six adjacent shafts and are thus suitable for the feed of very large bales or a large number of bales at one time.

After debaling, the material passes through initial size reduction units to separation and selection operations. Most size reduction tasks can be performed by the following machines: shredder, cutter or guillotine, screw shredder, and granulator.

6.11.2.1 Shredder

Shredders have been in use for a long time in many sectors for the recovery of scrap. To a large extent they draw in the material automatically, and are suited for film, sheets, solid pieces, hollow items, cables, etc. The stresses caused by the tough and partly high-strength material are enormous. Extremely sturdy units designed for this technology are thus required for the treatment of plastics. It is important that the cutting shafts run at a suitable speed so that cutting and tearing processes occur.

Models of shredders are offered with from one to six cutting shafts. Machines with a capacity of many tones per hour are available. They are able to reduce complete bales of film fed by forklift without any difficulty. Also, hollow items such as rubbish bins and barrels can be reduced when a ram is fitted to the feed. Another field of application is the shredding of cables to allow the separation of plastics and metal. Generally, a trough fed by a forklift or conveyor is located above the shredder shafts. After the material is reduced to a practical size in the shredder, it is transported to subsequent process stages by means of a conveyor or other mechanical device.

6.11.2.2 Cutter or Guillotine

Some plastics scraps are not suited for initial reduction in a shredder described above. These include fibers, long pieces of material, rolled strips, and lumps of rubber. A guillotine is better for these applications.

The material is fed manually in a trough or on an open conveyor to the guillotine. The latter operates as opposed to the shredder, on a stroke principle. A cutter, usually hydraulically operated, is lowered from above to cut the material in slices of the desired thickness. The complete cutting process including the material feed is best operated a programmed control.

6.11.2.3 Screw Shredder

The screw shredder mentioned earlier as a machine for debaling is also used for the initial size reduction of plastic items, and in particular when these are very voluminous and not too tough. It is suited for very large items or bundles of material and has the advantage of being fitted with a very large feed hopper that can be filled by bucket loader or similar device.

The machine is fitted with two shafts, rotating independently. It can be constructed, however, with up to six adjacent screw shafts, each shaft having its own drive via gears and electric motor. The shafts are equipped with shredder teeth for reducing the feed material in a crushing and tearing process. Not being a cutter, the machine is best suited for materials that can be broken or torn. When overloaded, a special control stops the respective shaft and switches it into reverse gear for a set time before returning to normal operation.

6.11.2.4 Granulators

Granulators can be seen as the most versatile size-reduction machine for the complete sector of plastics size reduction, and are used for the dry reduction of plastics. The machines used for this application are therefore designed to meet the special demands of job conditions, which are sturdy mechanical design, quick knife replacement, easy cleaning, and high capacity.

Since the reduction process is subject to the generation of a considerable amount of heat, it is necessary to water-cool parts of the machine or remove the heat with it. It is advantageous to fit the granulator with an open or semiopen rotor and a strong suction device to ensure that the grinding chamber is cooled intensively so that water-cooling is not required and the air is used at the same time for discharging the size-reduced material. All granulators should be equipped with a screen that can be easily removed. The screen opening determines the top size limitation of the size-reduced product. Material is fed to a feed hopper manually, or on a feed conveyor, screw, or similar device.

As an example, all granulators supplied by Herbold GmbH Maschinenfabrik (Meckesheim, Germany) have the following characteristics: (1) welded steel construction; (2) externally mounted bearings; (3) hinged two-piece housing with split point around the shaft; (4) easily replaceable screen; (5) double cross-cutting action; and (6) preadjustable knives. These characteristics offer a number of advantages, as explained below.

Due to the welded construction, the machine is resistant to extreme stresses caused by any foreign matter that may enter the granulator despite all precautionary measures taken, and fractures are avoided although the housing may be deformed. As the bearings are mounted outside the granulator housing, it is not possible for the feed material to enter the bearings or for grease to contaminate the material. The hinged housing allows easy and quick cleaning necessary when feed is changed and simplifies servicing and knife replacement. This is a significant advantage particularly in scrap recycling, where increased wear and more frequent knife replacement are to be reckoned with. For double cross-cutting action, all knives on the rotor are mounted at an inclined angle in a straight line to the rotor axis while all bed knives are set at the same angle but in an opposed inclined direction, also in a straight line. Complete sets of resharpened rotor- and bed-knives can be readjusted to the exact gap required between them to achieve the desired reducing action. This advantage, in conjunction with the good accessibility due to hinged housing, allows knife replacement to be carried out very quickly.

6.11.2.5 Fine Grinding

Fine grinding also offers solutions for the recycling of plastic scrap. Different types of machines are used, two common types being universal blast mills and disc pulverizers. In a universal blast mill, plastic scrap is reduced between the beater wings of a blast disc and a screen or the grooved grinding track of a grinding chamber. The hole size of the screen determines the fineness of the plastic powder. This usually has an upper size limitation of 500–800 μm .

In an impact disc pulverizer, which has much lower power consumption than the blast mill, the material is size reduced to an upper limit of about 800 μm between a fixed and a rotating disc. If a lower top size limitation is required, a screener may be used to return the coarse material continuously to the grind process. The finely ground powder is separated in a cyclone.

6.11.3 Cleaning and Selection

Cleaning, separation, and selection operations that usually follow the initial size reduction are determined by the type of recycling process to which the material is to be subjected. Basically there are two main recycling processes: recycle of heterogeneous plastics and recycle of selected polymers. The former process leads to the manufacture of extruded or injected products by direct reuse or in mixture with other components. The latter process consists of separation of the mix of collected plastics into homogeneous fractions, subjected to further processing that brings their characteristics and purity as near as possible to those of the original polymers.

The simplest method to perform the cleaning and selection operation consists of a selection platform where a number of trained sorters separate the different types of plastics on the basis of visual assessment. Though this is a hard and unpleasant job, the advantage of manual selection is that sorters operate to a degree of intelligence that the automatic equipment cannot reach. On the other hand, manual selection is, understandably, always liable to human error. To counter this problem, selection platforms are often equipped with detectors to check the quality of the selected material. These may be electronic appliances capable of recognizing, for example, PET in flux of PVC and vice versa, and detectors able to identify traces of metal overlooked during manual sorting, such as aluminum from caps and rings. The material manually selected and then electronically checked is therefore of best quality and can be sold at the maximum market price.

The most serious drawback of manual platforms lies in the high cost of labor and the need to manage a large number of workers when considerable quantities of material are to be sorted. Such drawbacks may be avoided by resorting to automatic platforms.

Automation is introduced at the stage of debaling. In order to obtain a product suitable for the recycling process, operations to remove undesired impurities must be carried out. The machines required are manifold and the necessity to employ them is related to the quality of the collected material. A few essential machines are: (1) rotary screen, by which parts of the desired dimension are sorted out, separating them from smaller and larger ones; (2) light-parts separation equipment, in which lighter parts such as films are separated by air blowing from the plastic material to be recycled; (3) heavy-parts separation equipment, in which heavy particles are separated and the operation is carried out by means of air that shifts the material selectively; and (4) aluminum rejection equipment, which normally consists of an electromagnetic drum placed in a suitable location on the train of operations. All such machines are preliminary to the stage of selection into homogeneous plastics fractions.

6.11.3.1 Dry Separation

The cleaning of plastics is often combined with the separation of other types of plastics and is performed by either dry or wet process depending on the quality of the collected material. A significant advantage of dry cleaning with air, as compared to wet cleaning, is that it has a lower power consumption. Loose adhering dirt—and this is the only type of sorting that can be removed in a dry process—is loosened and pulverized by the impact and rubbing caused during size reduction. The dirt, then as dust, can be separated by using an appropriate equipment. Examples of this are screen units and air stream separator.

The screen unit is the most economical means of removing the dirt. By selecting a screen with suitably sized openings, it is possible to minimize the amount of plastic discharged with the dust. Electrostatic charge can however cause too many dust particles to adhere to the plastic. The air separator (Figure 6.18) is then the more suitable device to use. Lighter-weight dust is carried out of the unit by the opposed directional air stream.

Mixed plastics, including various types of composite materials, that are to be dry-separated are first size-reduced (e.g., in a granulator) before the different constituents are separated. The separation is done in a process based on differences in material densities or shape and size of particles.

Screening may follow size reduction, depending on the material and the particle size distribution. In the screen unit, all of the mixed material is divided into two or three size fractions, e.g., 0–2, 2–4, and 4–6 mm. This is necessary since small heavy particles and large light pieces behave in the same manner, as do heavy flakes and light conical pieces. The separation based on density difference is easier or only then possible when all particles are of similar size.

Dry separation using air can be repeated several times, and the process is then classified as a cascade separator. A cascade separator, also known as a zigzag separator, uses an air stream passing through a rectangular zigzag channel from below (Figure 6.19). The material to be separated is fed to the top end of the channel into the air stream. The separation point is set by adjusting the air-flow rate. Material turbulence occurs in each section of the air stream channel, with lighter material being carried upward by air stream to discharge and heavy material moving downward from step to step. Fine particles are loosened from the larger ones and also from each other each time impact with side wall occurs. Cascade separators produce more efficient separation than single-stage units due to dispersion taking place at

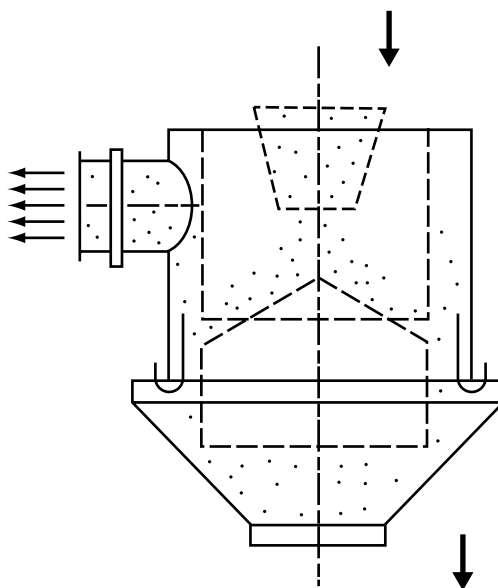


FIGURE 6.18 Schematic of air-stream separator.

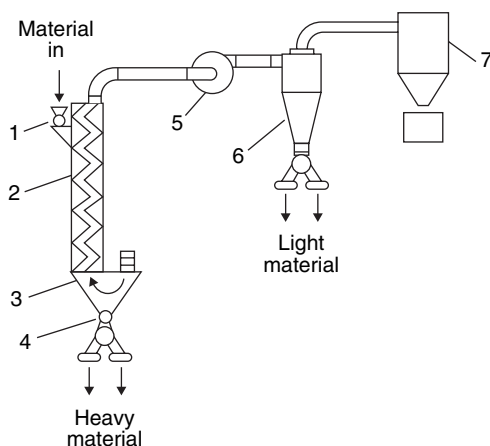


FIGURE 6.19 Schematic of air-stream (cascade) separator. 1, Gate valve; 2, cascading (zigzag) channel; 3, container with air suction; 4, gate valve; 5, blower; 6, cyclone; 7, filter with particle container.

each kink in the channel. Typical applications for the cascade separator are the separation of fibers and insulation film or foam and soft film.

The principle of operation of a fluidized air bed separator is shown in Figure 6.20. The material to be separated is carried uphill by the orbital vibration in the separation channel designed with a rectangular cross-section. An adjustable air stream is passed through the sieve surface in the channel where it lifts the material. The particles that are lifted higher in the air stream (that is, jump higher due to elasticity) flow downhill and are discharged from below. This type of fluidized air bed separation process can also be enhanced by using a multistage plant. A typical application for this unit is the separation of rubber from rigid thermoplastics or aluminum from plastics.

6.11.3.2 Wet Separation

Wet separation of plastics is a *microseparation method* in which a suspension medium is used to separate plastics with density higher or lower than the suspension medium. For example, water can be used as medium to separate PE from PVC or PET. In this case, special tanks are used in which various types of plastic flaks are mixed with water and then given a sufficient time to position themselves in the most suitable way according to their density. Materials are subsequently extracted separately from the top or bottom. This method is, however, not suitable for separating PVC from PET, because they have similar density.

Researchers at Rutgers University [70] studied a method of PVC microseparation from PET, by which PVC is subjected to a process of selective bulking that causes it to float. Such a method may be applied for separating small quantities of PVC from large quantities of PET, as normally is the case in the U.S., but is

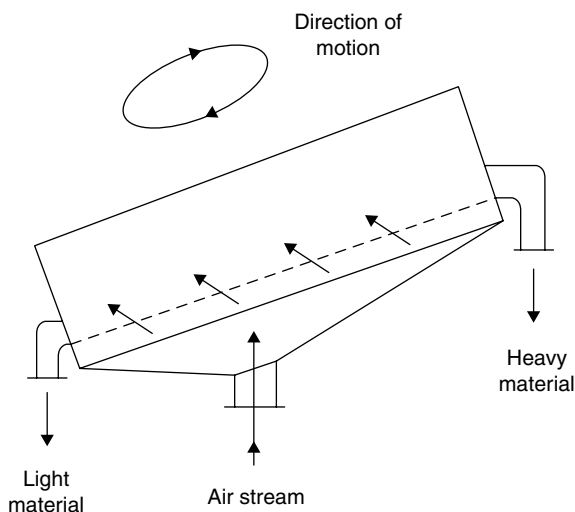


FIGURE 6.20 Schematic of vibrating air separator.

not suitable when PVC is a major component of the containers mix. Another wet method applicable to PVC and PET containers, previously reduced to flakes, is flotation with surface active agents.

6.11.3.3 Other Methods

Need for using microseparation techniques arises in critical situations where minute concentrations of identified contaminants adversely affect the post-consumer resin's usefulness in high-value end-uses. In many cases, microseparation, or the ability to sort resins by type, can be accomplished by air elutriation techniques (e.g., dry separation techniques and described above), wet separation techniques (such as sink/float tank technologies and hydrocyclones), magnets, electrostatic and electrodynamic methodologies, and optical scanners. Air aspiration and elutriation systems work well for separating light-density foams and films from denser reground plastics, while density-based methods are better for separating polyethylene from PET and denser resins.

Challenges to separate materials having similar densities, for example, PVC from PET regrind, or polypropylene from polyethylene, remain. Examples of microsorting techniques commercialized so far include electrostatic separation devices designed to sort by way of resin's conductivity, supercritical fluids which alter the separation fluid's density, froth flotation using the alteration of a liquid's surface tension to separate various solids, and chemical dissolution based on the difference in solubility of various plastics in selective solvents. Another development is a novel method to separate diverse resins by taking advantage of their differences in stick temperature.

BASF's Kali and Salz AG company, which has extensive experience in electrostatic separation of salts, employs its own electrostatic separation process (ESTA) to the separation of plastics. Using density separation, paper and plastic residues from labels and crowns are separated first. Then, following pretreatment with surface active substances designed to enhance the electrostatic properties, the homogeneously milled particles are charged electrically as they rub against each other. The extent of electrostatic charge depends on the plastic. The particles then fall through a high-tension field and are diverted at different angles depending on the charge, resulting in separation.

6.11.4 Resin Detectors: Type and Configuration

Detectors fall into four categories—x-ray, single-wavelength infrared (IR), full-spectrum IR, and color. The earliest automated systems used x-rays, which are still the most effective means of determining the presence of PVC. The chlorine atom in PVC emits a unique signal in the presence of x-rays by either x-ray transmission (XRT) or x-ray fluorescence (XRF). The XRT signal passes through the container, ignoring labels and other surface contaminants, and is capable of detecting a second container that may be stuck to the first. XRF, on the other hand, bounces off the surface of the container and is useful for finding any PVC, including labels and caps.

Systems for separating multiple types of plastics utilize a single wavelength of the near-infrared (NIR) spectrum. These systems work on the basis of a simple determination of opacity and separate the stream of mixed containers into clear (PET and PVC), translucent (HDPE and PP), and opaque (all pigmented and colored materials) streams.

The most sophisticated detectors, however, employ full spectrum NIR. Since all plastics absorb IR to different degrees and each resin has a unique "fingerprint," these detectors can accurately separate each of the resins. In later developments, filters for individual wavelengths are used for rapid identification and there is promise for even faster, lower-cost systems.

The color detectors are, in fact, very small cameras capable of identifying a number of colors. When combined with a resin-specific detector, they allow a variety of sorts based on both resin type and color.

Containers must be separated and presented to a detector in order to collect data on each unit. That information is then integrated via computer, and the container is tracked down the conveyor until it reaches the appropriate ejection point, where it is removed by a timed blast of air. The two primary

techniques for presenting containers to a detector are full-conveyor or single-file systems. Containers delivered in a full-conveyor system can achieve higher throughput rates and are normally used to remove a single material from the mixture. A singulated stream, on the other hand, has lower throughputs, but allows sorting into a number of streams on a single pass.

Detectors are usually arranged in one of three configurations. The first is single detector/single container (Figure 6.21a): this is the simplest setup for singulated containers. As each container passes the detector, several readings are taken instantaneously and a decision is made by the computer. While usually accurate, this process is subject to error if the container has a large label blocking the signal and thus restricting data input to the computer. The second configuration is multiple detector/single container (Figure 6.21b): as each container passes the detector assembly, it is read by a number of detectors resulting in a more accurate reading. The third is multiple detector/multiple container (Figure 6.21c): This is the standard configuration for a mass-flow system and has detectors spaced to cover the width of the conveyor. When the target material is spotted, its position on the belt is noted and accordingly an ejector removes it before falling off at the end of the belt.

Further development in autosort technology is represented by particulate-sorting units capable of sorting by color. Applied in combination with the aforesaid resin detectors this facilitates autosorting according to both resin-type and color.

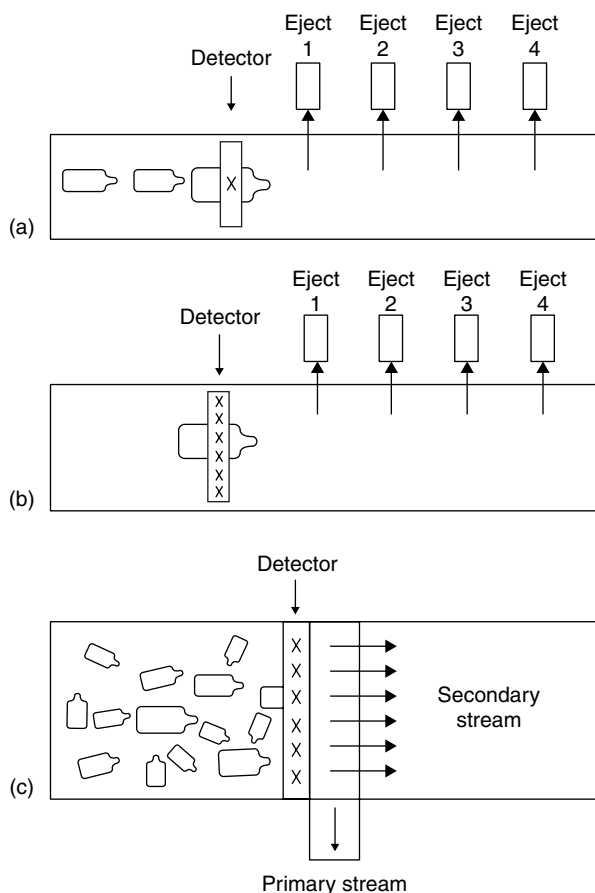


FIGURE 6.21 Typical separation and sorting setups using three main detector systems: (a) single detector/single sample; (b) multiple detector/single sample; and (c) multiple detector/multiple sample. (After Tomaszek, T. 1993. Automated Separation and Sort, *Modern Plastics*, 34–36 (November).)

6.11.5 Automatic Sortation

Most end-use markets of recycled plastics require that they be separated by resin type and color. For post-consumer bottles, all lids, caps, and closures should also be removed because they are often of different colors, and made of different resins than the bottle. The goal of any sorting process is to obtain the highest purity, consistency, and quantity of a particular consumer resin type. This ensures the highest end-use value for new products incorporating substantial amounts of the recycled resin.

In the widely used manual method of sorting, employees known as material handlers are stationed at predetermined locations alongside the sort conveyor to remove the desired bottles for recycling. All caps and closures still affixed to the bottles are manually removed by the handlers prior to or during sorting. These manual methods of sorting, however, face many challenges, some of which are economic and others environmental and aesthetic. Among the key hurdles are high cost of the labor-intensive process, exposure of employees to the residual household and industrial chemicals contained in some of the collected bottles, difficulty in sorting look-alike resins, and subjective material quality standards resulting from manual sorting. Automating the container sorting process to overcome these hurdles has thus been a major goal of the recycling industry.

An automatic separation process that includes various systems employing detectors currently available in the market is ideally suited to *macroseparation* or *macrosorting* (separation of plastic fractions before size reduction) when waste materials are still in the initial form (such as post-consumer bottles). Macrosorting is one of the fastest-growing segments of the plastics recycling industry. Although automated sorting, by resin type and color, can be accomplished after size reduction, most commercial automated-sorting machines are designed to sort plastics containers in whole form before size reduction. Some of the automated bottle-sorting systems are designed to sort certain bottles such as look-alikes, while others are designed to separate all plastics bottles by resin type and color. The most commonly encountered look-alike bottles are those fabricated from nonpigmented PVC and clear PET.

6.11.5.1 PVC/PET and Commingled Plastics Sortation

Both PVC and PET bottles are very recyclable. However, when the two types are received commingled, the reprocessor can experience quality deficiencies due to rheological incompatibilities between these two resins. This has been of special concern to the PET bottle reclaimer because, as the PET is heated to its processing temperature, trace amounts of PVC can cause severe deterioration in the quality of the reprocessed PET resin. Therefore the two resins must be separated prior to recycling.

Manual sorting of look-alike PVC and PET cannot meet the market's needed quality. Therefore new techniques have been engineered that will detect and separate bottles made from either of these two resins. The first detector was developed by Tecoplast in Casumaro, Ferrara-Italy, to separate PVC from PET. The application of this system resulted in the introduction of an automatic plant, processing drink plastic bottles using the AZZURRA machine. The Tecoplast detector consists of an x-ray source and a receiver that measures the bottle absorption while passing between the source and receiver. PVC has a higher absorption compared to the other plastic due to the presence of a chlorine atom. The value of PVC absorption, electronically processed through algorithms, makes it possible to detect its presence and consequently to eject bottle.

Another detector is employed to line up bottles using a suction robot. The aligning process enables bottles to be arranged in a suitable way for measuring transparency and color. Using this technology, Tecoplast developed the first optical detector capable of establishing the quality of PET, thus allowing the separation between clear PET and colored PET, besides the aforesaid separation from PVC. In a later development, Govoni's technology employed detectors performing these separations without alignment.

Other detectors have been developed in the U.S. A leading manufacturer of plastics sortation equipment, ASOMA Instrument Inc. (Austin, TX), developed a simple operator-friendly device for sensing the presence of chlorine atoms contained within the PVC resin. This sensor identifies PVC by x-ray fluorescence as bottles fall through a chute or move on a belt conveyor, at the end of which either the PVC or PET bottles are extracted—in most cases, by a burst of compressed air-jet actuated by the

device, although mechanical devices have also been employed. The x-ray fluorescence sensitivity is so reliable that a 10 ms analysis is all that is needed to make proper selection. Single-unit systems have been developed that both detect and separate commingled bottles at production rates of 800–1200 lb/h, which corresponds to between two and three bottles per second. As is the case with most macroseparation devices, singulation (that is, alignment of bottles in a single file) is critical for this system to function at high production rates while maintaining rigorous quality standards. With x-ray detection, sorted PET streams having less than 50 ppm of PVC have been consistently produced, while, in contrast, manual separation generally results in PET with 2000 ppm PVC [71].

Another example is a system made by National Recovery Technologies (NRT) Inc. (Nashville, TN) [72]. This apparatus incorporates a proprietary electromagnetic screening process that also detects the presence of chlorine as found in PVC bottles. Once detected, PVC bottles are pneumatically jettisoned from the commingled bottle feed stream by a microprocessor-based air-blast system. The NRT technology permits bottles to be delivered to the unit in a mass sort concept in either crushed or whole form. This system does not require any special positioning or orientation of the bottles in order to achieve high efficiency rates.

An optical detector developed by Magnetic Separation Systems (MSS) Inc. (Nashville, TN) incorporates an optical sensing device with a transmission output range of 200–1500 nm to detect both the resin composition and the shape of the inspected container. Additionally, a video camera is employed to identify colored containers via computerized spectrographic matching. This information is also processed through a high-speed microprocessor that has the ability to perform algorithmic analyses and alarm the programmable logic controller (PLC) to actuate an ejection apparatus to sort the desired bottle. Finally, an x-ray fluorescence sensor is used to sort PVC bottles from the PET bottle fraction. The MSS detector system is thus designed to obtain separation of commingled plastics into homogeneous material fractions, including PVC, clear PET, colored PET, multicolored HDPE, and translucent HDPE.

A modular sorting system of MSS, BottleSort, Incorporates a sensory apparatus designed to detect and mechanically separate commingled plastic bottles in a process that includes several functions: debaling, screening, sensing, separation, and electronic control. Sensing is performed both optically and with x-ray fluorescence. Each BottleSort modular unit can process 1250 lb/h. Systems have been commercially installed incorporating four units having a combined capacity to sort 5000 lb of commingled bottles each hour.

A near-infrared spectrophotometry detector, developed by Automation Industrial Control (AIC) of Baltimore, MD, allows identification of resin type, such as PET, HDPE, PVC, PP, LDPE, and PS. The equipment is connected with another detector for color determination and the resulting data are processed by computer with highly sophisticated software. The equipment thus enables separation of a container mix into various components with a high degree of selectivity in regard to typology and color. This type of detector, however, requires material singularization and lining up.

The PolySort automatic plastic bottle sorting system introduced by AIC is designed to receive commingled plastic bottles in either baled or crushed form. At the heart of this sorting system is a sophisticated video camera and color monitor incorporating a strobe to detect and distinguish colors in the inspected plastic bottle. This optical scanning device interfaces with a computer to match the color of the bottle against a master. The detector is reputed to detect and match up to 16 million shades of colors. In addition, the system can be programmed to disregard labels on the bottles. Following color detection, a near-infrared detection system scans the single-bottle stream at a rate of approximately 3000 times a minute, to determine in less than 19 ms the primary resin found in each one. This is achieved by matching the interferogram produced by the bottle to a known master for each base resin as stored in the system.

Computations are coordinated through the use of a rotary pulse generator and sensing light curtain to impel the qualified bottle to a discharge chute located on the sort conveyor. Although the standard PolySort system is designed to detect and sort about 1500 lb of compacted bottles each hour, higher production rates can be obtained by feeding multiple lines from one debaler.

A point of consideration is the efficiency of separation that could nullify the high efficiency of a detection equipment. Detection must be unfailingly followed by rejection of the detected bottle, and in reality this does not always occur. Delivery systems in use today are effective but not 100% accurate. Most errors that occur with an autosort process are due to mechanical delivery errors rather than error related to detection. Therefore, a check on the operations of selection of the detected product is of primary importance. Detectors with 99% or greater efficiency, if installed in series and in number of at least two units, can bring the level of impurities within the limits required. For example, with a mix in the proportion of 90% PET and 10% PVC, two detectors with 99.5% efficiency placed in series enable one to obtain a level of impurities of 2.5 ppm, whereas with efficiency of 99% the value of residue is 10 ppm.

6.11.6 Recycle Installations

Special importance is generally attached to the techniques of electronic selection of homogeneous fractions, as discussed above, while disregarding the phase of regeneration of selected plastics. This would be justified if plastics articles were manufactured following criteria of perfect recyclability. However, such criteria are not yet universally adopted or followed. Therefore, an accurate response must be given, in any recycling plant design, to the problems posed by various elements that normally compose the item to be recycled. Referring to liquid containers, in general, these consist of, in addition to the body made of plastics, other foreign bodies that are to be removed. Such elements may be caps made of PE, PE with PVC gaskets, aluminum, labels of PVC or tacky paper with different types of glue, and residues and dirt that may have been added during the waste-collection phase.

Various operations, to be carried out in a specific sequence because of the problems posed by the type of material, are grinding, dry separation, and wet separation. Machineries to be installed for these operations are dictated by the typology and quality of recycle items.

Grinding is the first step following selection and requires attention and accuracy in design to ensure optimum homogeneity of the ground product. Several types of grinding equipment in common use have been described earlier.

The purpose of dry separation is the removal of a part in the dry phase. The process allows avoiding problems of dissolution in water and relevant contamination. An air flotation method is used for dry separation. Specially designed machines combining the effects of vibration and air flotation ensure separation of flakes with different specific weight. Such machines are very useful for removal of parts of labels that were freed by grounding. An extremely interesting application of this method is the separation of PVC labels from PET bottle flakes.

Residues are normally washed out of material flakes using a class of equipment that includes centrifugal cleaners, washing tanks, autoclaves, settling tanks, combined-action machines, scraping machines (mechanical friction), and centrifugal machines (for water separation). The construction details of the machinery and their installation according to a specific sequence are in the know-how of various manufacturers and very little is revealed. In view of complex problems posed by post-consumer plastics installations, it may, however, be said that it is not possible to expect miraculous results from key processes carried out in a single passage and therefore the efficiency is maximized by repetition of the same operation in more than one phase.

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A1

Trade Names for Some Industrial Polymers

Trade Name	Company	Type of Polymer
Abson	B. F. Goodrich	Acrylonitrile–butadiene–styrene terpolymer
Aclar, Aclon	Allied	Polychlorotrifluoroethylene
Acraldon	Bayer	Ethylene–vinyl acetate copolymers
Acrylan	Monsanto	Acrylic fiber
Acrylite	Cyanamid/Rohm	Acrylic resin
Acrypanel	Mitsubishi	Poly(methyl methacrylate)
Adiprene	Du Pont	Polyurethanes
Afcoryl	Pechiney–Saint-Gobain	Acrylonitrile–butadiene–styrene terpolymer
Aflas	Asahi Glass	Tetrafluoroethylene–propylene + cure site monomer terpolymer
Aflon	Ashai Glass	Tetrafluoroethylene–ethylene copolymer
Akulon	Akzo	Nylon-6
Alathon	Du Pont	Low-density polyethylene
Algoflon	Montedison	Polytetrafluoroethylene
Alkathene	ICI	Low-density polyethylene
Alkox	Meisei Chemical Works	Poly(ethylene oxide)
Alloprene	ICI	Chlorinated natural rubber
Alpolit	Hoechst	Unsaturated polyester resins
Amberlite	Rohm & Haas	Ion-exchange resin
Ameripol-CB	B. F. Goodrich	Polybutadiene
Amidel	Union Carbide	Transparent amorphous Polyamide
Amilan, Amilon	Toray	Nylon-6
Antron	Du Pont	Polyamide fiber
Araldite	Ciba–Geigy	Epoxy resin
Ardel	Union Carbide	Polyarylate
Arnite	Akzo	Poly(ethylene terephthalate)
Arnite E	Akzo	Thermoplastic polyester elastomers
Arnite PBTP	Akzo	Poly(butylenes terephthalate)
Arnitel	Akzo	Thermoplastic polyester elastomer
Arotone	Du Pont	Polyaryletherketones (PEEK)
Arylef	Solvay	Polyarylate
Arylon	Du Pont	Polyarylates
Astrel	3M	Polyarylsulfone
Avimid	Du Pont	Polyimide

(continued)

Trade Name	Company	Type of Polymer
Bayblend	Bayer	Polycarbonate/ABS blend
Baygal, Baymidur	Bayer	Polyurethane casting resins
Baylon	Bayer	Polycarbonate
Baypern	Bayer	Polychloroprene
Beetle	British Industrial Plastics	Urea-formaldehyde resin
Benvic	Solvay	Poly(vinyl chloride)
Bipeau	Ato Chimie	Poly(vinyl chloride) (PVC)
Blendex	G.E.	Acrylonitrile-polybutadiene-styrene graft copolymers
Budene	Goodyear	Polybutadiene
Buna-N	Chem. Werke Hüls	Butadiene-acrylonitrile copolymer
Buna-S	Chem. Werke Hüls	Butadiene-styrene copolymer
Butacite	Du Pont	Poly(vinyl butyral)
Butakon	ICI	Butadiene copolymers
Butaprene	Firestone	Styrene-butadiene copolymers
Butvar	Shawinigan	Poly(vinyl butyral)
BXL	Union Carbide	Polysulfone
Cabelec	Cabot	Ethylene-vinyl acetate copolymers
Caprolan	Allied	Polyamide fiber
Capron	Allied	Polyamide resin
Caradol	Shell	Polyhydroxy compound for isocyanate cross-linking
Carbopol	B. F. Goodrich	Acrylic polyelectrolyte
Carboset	B. F. Goodrich	Acrylic polyelectrolyte
Carbowax	Union Carbide	Poly(ethylene oxide)
Cariflex I	Shell	<i>cis</i> -1,4-polyisoprene
Carina	Shell	Poly(vinyl chloride)
Carinex	Shell	Polystyrene
Cebian	Daicel	Styrene-acrylonitrile copolymers
Celanex	Celanese	Poly(butylene terephthalate)
Celcon	Celanese	Polyacetal
Cellioder B	Bayer	Cellulose acetate-butyrate
Cellit	Bayer	Cellulose acetate
Cellon	Dynamit-Nobel	Cellulose acetate
Cellosize	Union Carbide	Hydroxyethylcellulose
Celluloid	Dynamit Nobel	Cellulose nitrate plasticized with camphor
Chemfluor	Norton/Chemplast	Polyvinylidene fluoride
Chemigum	Goodyear	Polyurethane rubber
Cibamin	Ciba-Geigy	Urea-formaldehyde, melamine-formaldehyde resins
Cibanoid	Ciba-Geigy	Urea-formaldehyde resin
<i>cis</i> -4	Phillips	<i>cis</i> -1,4-polybutadiene
Clariflex TR	Shell	Styrene-diene-styrene triblock elastomer
Cobex	Bakelite Xylonite	Poly(vinyl chloride)
Colcolor	Degussa	Ethylene-vinylacetate copolymers
Coral	Firestone	<i>cis</i> -1,4-polyisoprene
Cordura	Du Pont	Polyamide fiber
Corvic	ICI	Poly(vinyl chloride)
Courtauld	Courtaulds	Polyacrylonitrile
Crastin	Ciba-Geigy	Poly(butylene terephthalate)
Craston	Ciba-Geigy	Polyphenylene sulfide
Creslan	Cyanamid	Acrylic fiber
Crofon	Du Pont	Poly(methyl methacrylate)
Crystic	Scott Bader	Polyester resins

(continued)

Trade Name	Company	Type of Polymer
Cyanaprene	American Cyanamid	Polyurethane casting resins
Cycolac	G.E.	Acrylonitrile–butadiene–styrene graft copolymers
Cymel	Cyanamid	Melamine–formaldehyde resin
Cyrolite	Röhm	Styrene–polybutadiene graft copolymers
Dacron	Du Pont	Poly(ethylene terephthalate) fiber
Daltocel	ICI	Rigid polyurethane foams
Daltoflex I	ICI	Polyurethane rubber
Dapon	FMC Corp.	Diallyl phthalate resins
Darvic	ICI	Poly(vinyl chloride)
De-acidite	Permutit Co.	Ion-exchange resin
Degaplast, Deglas	Degussa	Poly(methyl methacrylate)
Delmer, Delpet	Asahi Chemical	Poly(methyl methacrylate)
Delrin	Du Pont	Polyacetal
D.E.R.	Dow	Epoxy resin
Desmobond	Mobay	Epoxide resins
Desmopan	Bayer	Thermoplastic polyurethane elastomers
Desmophen	Bayer	Rigid polyurethane foams
Desmophen A	Bayer	Polyurethane rubber
Diakon	ICI	Poly(methyl methacrylate) molding powder
Diene	Firestone	Polybutadiene
Diofan	BASF	Vinyl chloride–vinylidene chloride–acrylonitrile copolymers
Diolen	ENKA-Glazstaff	Poly(ethylene terephthalate)
Dobeckot	BASF	Epoxide resins
Doctolex	Mitsubishi	Polyaryletherketones (PEEK)
Dorlastan	Bayer	Spandex fiber
Dowex	Dow	Ion-exchange resin
Dowlex	Dow	LLDPE
Duolite	Chemical Process Co.	Ion-exchange resins
Duracon	Daicel Polyplastics	Polyacetal
Durel	Hooker	Polyarylate
Durethan	Bayer	Nylon-6
Durethan A	Bayer	Nylon-6,6
Durethan B	Bayer	Nylon-6
Durethan U	Bayer	Thermoplastic polyurethanes
Durez	Occidental Chemical Corp.	Phenol–formaldehyde resins
Dutral	Montecatini	Ethylene–propylene copolymer
Dycryl	Du Pont	Photopolymer system
Dyflor	Dynamit Nobel	Poly(vinylidene fluoride)
Dylene	Arco Chemical	Styrene homopolymers
Dynel	Union Carbide	Vinyl chloride–acrylonitrile copolymer
Dynyl	Rhone-Poulenc	Elastomeric polyamides, copolyamides
Eccofoam	American Micro	Rigid polyurethane foam
Ecdel	Eastman Chem. Products	Thermoplastic polyester elastomer
Econol	Carborundum	Poly(<i>p</i> -hydroxybenzoic acid ester)
Ekcel	Carborundum	Aromatic polyester
Ekonol	Carborundum	Polycarbonate
Ektar	Eastman Chem. Intern.	Polyphenylenesulfide
Elvacet	Du Pont	Poly(vinyl acetate)
Elvanol	Du Pont	Poly(vinyl alcohol)
Elvic	Solvay	Poly(vinyl chloride)
Encron	Akzo	Polester fiber
Ensolute	Uniroyal	Poly(vinyl chloride)

(continued)

Trade Name	Company	Type of Polymer
Epicote	Dow	Epoxide resins
Epodite	Showa Highpolymer	Epoxide resins
Epon	Shell	Epoxide resins
Epi-Rez	Celanese	Epoxide resins
Escor	Exxon	Ethylene–vinyl acetate copolymers
Escorene	Exxon	Polyethylenes
Eska	Mitsubishi	Poly(methyl methacrylate)
Estamid	Upjohn	Nylon-12 elastomers
Estane	B. F. Goodrich	Thermoplastic polyurethane elastomer
Estar	Eastman Kodak	Polyester film
Etar	Eastman Chem. Intern.	Polyethylene terephthalate
Ethocel	Dow	Ethylcellulose
Evatane	Ato Chimie	Ethylene–vinyl acetate copolymers
Evatate	Sumitomo	Ethylene–vinyl acetate copolymers
Extrel	Exxon	Polypropylene
Fertene	Himont	Polyethylenes (HD, LD)
Fiberloc	B. F. Goodrich	Poly(vinyl chloride)
Flemion	Asahi Glass	Carboxylated fluoropolymer
Flovic	ICI	Poly(vinyl acetate)
Fluon	ICI	Polytetrafluoroethylene
Fluorel	3M	Vinylidene fluoride– hexafluoropropylene copolymer
Foraflon	Ato Chimie	Polytetrafluoroethylene
Formica	Cyanamid	Melamine–formaldehyde resin
Forticel	Celanese	Cellulose propionate
Fortron	Hoechst	Polyphenylenesulfide
Gafite	Hoechst	Poly(butylenes terephthalate)
Gaflex	Hoechst	Thermoplastic polyester elastomers
Gaftuf	Hoechst	Poly(butylenes terephthalate)
Gecet	G.E.	Polyphenylene ether
Geloy	G.E.	Styrene–acrylonitrile copolymers
Gelvitol	Shawinigan	Poly(vinyl alcohol)
Genal	G.E.	Phenol–formaldehyde resins
Genopak, Genotherm	Hoechst	Poly(vinyl chloride)
Geon	B. F. Goodrich	Poly(vinyl chloride)
Grilamid	Ems Chemie	Nylon-12
Grilamid ELY 60	Ems Chemie	Polyamide elastomers
Grilamid TR	Emser Werke	Transparent amorphous polyamide
Grilon	Ems Chemie	Nylon-6
Grilonit	Ems Chemie	Epoxide resins
Grilpet	Ems Chemie	Poly(ethylene terephthalate)
Halar	Ausimont	Ethylene–chlorotrifluoroethylene copolymer
Halon	Ausimont	Polytetrafluoroethylene
Herculoid	Du Pont	Cellulose nitrate
H-film	Du Pont	Polyamide from pyromellitic anhydride and 4,4'-diaminodiphenyl ether
Hi-fax	Hitachi	Polyethylene
Hitalex	Hitachi	Polyethylene
Hostadur	Hoechst	Poly(ethylene terephthalate)
Hostaflon ET	Hoechst	Tetrafluoroethylene–ethylene copolymer
Hostaflon FEP	Hoechst	Tetrafluoroethylene– hexafluoropropylene copolymer
Hostaflon TF	Hoechst	Polytetrafluoroethylene
Hostaflon TFA	Hoechst	Perfluoroalkoxy copolymers

(continued)

Trade Name	Company	Type of Polymer
Hostaform	Hoechst	Polyoxymethylene
Hostalen	Hoechst	Polyethylenes (HD, LD)
Hostalen GUR	Hoechst	Ultrahigh-molecular weight polyethylene
Hostalen PP	Hoechst	Polypropylene
Hostalit	Hoechst	Poly(vinyl chloride) and blends
Hostamid	Hoechst	Transparent amorphous polyamide
Hostatec	Hoechst	Polyether ketone
Hycar	B. F. Goodrich	Polyacrylate
Hydrin	B. F. Goodrich	Epichlorohydrin rubber
Hylar	Du Pont	Poly(ethylene terephthalate)
Hypalon	Du Pont	Sulfochlorinated polyethylene
Hytrel	Du Pont	Thermoplastic polyester elastomers
Hyvis	BP Chemicals	Polyisobutylene
Icdal Ti40	Dynamit Nobel	Polyesterimide
Impet	Hoechst	Poly(ethylene terephthalate)
Ionac	Ionac Co.	Ion-exchange resins
Irrathene	G.E.	PE, cross-linked by radiation
Isonol	Dow	Rigid polyurethane foams
Ixan	Solvay	Vinyl chloride–vinylidene chloride–acrylonitrile copolymers
Ixef	Solvay	Aromatic polyamide
Jupilon	Mitsubishi	Polycarbonate
Kadel	Amoco	Polyaryletherketones (PEEK)
Kalrez	Du Pont	Fluoroelastomer
Kamax	Rohm & Hass	Polyacrylic esterimide
Kapton	Du Pont	Polyimide film
Kardel	Union Carbide	Styrene homopolymers
Kel-F	3M	Polychlorotrifluoroethylene, poly(vinyl fluoride)
Kel-F elastomer	3M	Vinylidene fluoride–chlorotrifluoroethylene copolymer
Kematal	Hoechst	Acetal homopolymers
Kermel	Rhone-Poulenc	Polyimide fiber
Kerimid	Rhone-Poulenc	Polimide
Kinel	Rhone-Poulenc	Polybismaleinimide
Kodapak	Eastman Chem. Intern.	Poly(butylenes terephthalate)
Kodar PETG	Eastman Chem. Intern.	Copolyester based on 1,4-cyclohexylene glycol and a mixture of terephthalic and isophthalic acids
Kodel	Eastman Chem. Intern.	Polyester fiber
Kralastic	Uniroyal	Acrylonitrile–butadiene–styrene copolymer
Kraton	Shell	Thermoplastic styrene block copolymer
Kuralon	Kuraray (Japan)	Poly (vinyl alcohol) fiber
Kynar	Pennwalt	Poly(vinylidene fluoride)
Laminac	Cyanamid	Polyester resins
Leguval	Bayer	Unsaturated polyester resins
Lekutherm	Bayer	Epoxide resins
Levapren	Bayer	Ethylene–vinyl acetate copolymer
Levasint	Bayer	Ethylene–vinyl alcohol copolymers
Lewatit	Bayer	Ion-exchange resins
Lexan	G.E.	Polycarbonate
Localen	BASF	Ethylene–vinyl acetate copolymers
Lomod	G.E.	Thermoplastic polyester elastomers

(continued)

Trade Name	Company	Type of Polymer
Lucite	Du Pont	Poly(methyl methacrylate) and copolymers
Lucryl	BASF	Poly(methyl methacrylate)
Lupolen	BASF	Ethylene–vinyl acetate copolymers
Luran	BASF	Styrene–acrylonitrile copolymers
Luranyl	BASF	Poly(ethylene oxide) blend
Lustran	Monsanto	Acrylonitrile–butadiene–styrene terpolymer
Lustrex	Monsanto	Polystyrene
Lycra	Du Pont	Spandex fiber
Makrolon	Röhm	Polycarbonate
Maplen	Himont	Polyethylenes (HD, LD)
Maranyl	ICI	Nylon-6
Maranyl A	ICI	Nylon-6,6
Marlex	Phillips	Polyethylene, polypropylene
Marlex TR 130	Phillips	Polyethylene (LLD)
Melinar, Melinite	ICI	Poly(ethylene terephthalate)
Melinex	ICI	Polyester film
Melopas	Ciba–Geigy	Melamine–formaldehyde resins
Merlon	Mobay	Polycarbonate
Methocel	Dow	Methyl cellulose
Minlon	Du Pont	Nylon-6,6
Moltopren	Bayer	Rigid polyurethane foam
Moplen	Himont	Polypropylene
Mowicoll	Hoechst	Poly(vinyl acetate) dispersions
Mowilith	Hoechst	Poly(vinyl acetate)
Mowiol	Hoechst	Poly(vinyl alcohol)
Mowital	Hoechst	Poly(vinyl butyral)
Mylar	Du Pont	Poly(ethylene terephthalate) film
Nafion	Du Pont	Persulfonated fluoropolymer
Nalcite	National Aluminate Corp.	Ion-exchange resins
Napryl	Pechiney–Saint-Gobain	Polypropylene
Natene	Pechiney–Saint-Gobain	Polyethylenes
Natsyn	Goodyear	Polyisoprene
Necofene	Ashland	Polyphenylene ether
Neosepta F	Tokoyama Soda	Ionic membrane (based on fluoropolymer)
Nikalet	Nippon Carbide	Epoxide resins
Nipoflex	Toyo Soda	Ethylene–vinyl acetate copolymer
Nipolon	Toyo Soda	Polyethylenes (HD, LD)
Nitron	Monsanto	Cellulose nitrate
Noblen	Mitsubishi	Polypropylene
Nolimid (adhesives)	Rhone-Poulenc	Polybismaleinimide
Nomex	Du Pont	Poly(<i>m</i> -phenylene isophthalamide)
Nordel	Du Pont	Ethylene–propylene–diene terpolymer
Noryl	G.E.	Poly(phenylene oxide)–polystyrene blend
Novadur	Mitsubishi	Poly(butylene terephthalate)
Novarex	Mitsubishi	Polycarbonate
Novatec	Mitsubishi	Polypropylene, polyethylenes (HD, LD)
Novatex	Mitsubishi	Polyethylene (LLD)
Novex	BP Chemicals	Polyethylenes (HD, LD)
Novodur	Bayer	Acrylonitrile–polybutadiene–styrene graft copolymers
Oppanol B	BASF	Polyisobutylene
Oppanol C	BASF	Poly(vinyl isobutyl ether)

(continued)

Trade Name	Company	Type of Polymer
Oppanol O	BASF	Copolymer from 90% isobutylene and 10% styrene
Orgalan	Ato Chimie	Polycarbonate
Orgamide	Ato Chimie	Nylon-6
Orgavyl	Ato Chimie	Poly(vinyl chloride)
Orlon	Du Pont	Acrylic fiber
Oroglas	Rohm & Haas	Poly(methyl methacrylate)
Paraglas	Degussa	Poly(methyl methacrylate)
Paraplex	Rohm & Haas	Epoxide resins
Parapol	Exxon	Polyisobutylene
Parlon	Hercules	Chlorinated rubber
Paxon	Allied	Polyethylene
Pebax	Ato Chimie	Polyamide elastomers
Pelaspán	Dow	Polystyrene (expandable)
Pelprene	Toyobo	Thermoplastic polyurethane elastomer
Perbunan N	Bayer	Butadiene–acrylonitrile copolymers
Perlenka	Akzo	Nylon-6
Permutit	Permutit Co.	Ion-exchange resins
Perspex	ICI	Poly(methyl methacrylate) sheet
Petlon	Mobay	Poly(ethylene terephthalate)
Petra	Allied Signal	Poly(ethylene terephthalate)
Petrothene	USI Chemical	Polyethylenes (HD, LD, LLD)
Pevalon	May & Baker	Poly(vinyl alcohol)
Plastazote	American Micro	Polyethylene foam
Plexiglas	Rohm & Haas	Poly(methyl methacrylate)
Plexigum	Rohm & Haas	Acrylate and methacrylate resins
Pliofilm	Goodyear	Rubber hydrochloride
Pliolite	Goodyear	Styrene–butadiene copolymers
Pliovic	Goodyear	Poly(vinyl chloride)
Pocan	Bayer	Poly(butylenes terephthalate)
Polybond	BP Chemicals	Ethylene–vinyl acetate copolymers
Polycal	Ato Chimie	Poly(vinyl chloride)
Poly-Eth	Gulf Oil	Polyethylene
Polymidal	Raychem	Polyimide
Polymin	BASF	Polyethyleneimine
Polyox	Union Carbide	Poly(ethylene oxide)
PolyPro	Mitsui Petrochemical	Polypropylene
Polysizer	Showa Highpolymer	Poly(vinyl alcohol)
Polythene	Du Pont	Low-density polyethylene
Polyviol	Wacker Chemie	Poly(vinyl alcohol)
Prevex	Borg Warner	Poly(phenylene oxide) blend
Prodorit	T.I.B. Chemie	Epoxide resins
Profax	Himont	Polypropylene
Propathene	ICI	Polypropylene
Pulse	Dow	(ABS + Polycarbonate) polymer blends
Pyralin	Du Pont	Polyimide
Pyre ML	Du Pont	Polyimide coating
Qiana	Du Pont	Polyamide fiber from bis(<i>p</i> -aminocyclohexyl)methane and dodecanedioic acid
Radel	Union Carbide	Polyether sulfone
Ravinil	EniChem	Poly(vinyl chloride)
Resolite	Ciba–Geigy	Urea–formaldehyde resin
Rilsan A	Ato Chimie	Nylon-12
Rilsan B	Ato Chimie	Nylon-11
Rimplast	Petrarch Systems	Silicone resins and molding compounds

(continued)

Trade Name	Company	Type of Polymer
Royalene	Uniroyal	Ethylene-propylene-diene terpolymer
Roylar	Uniroyal	Polyurethanes
Roylar	B. F. Goodrich	Thermoplastic polyurethane elastomers
Rucon	Hooker	Poly(vinyl chloride)
Rucothane	Hooker	Polyurethanes
Rynite	Du Pont	Glass-reinforced poly(ethylene terephthalate)
Ryton	Phillips	Polyphenylenesulfide
Santolite	Monsanto	Polyaryletherketones
Santoprene	Monsanto	Modified polypropylene
Saran	Dow	Copolymers of vinylidene chloride, vinyl chloride and acrylonitrile
Scotchcast	3M	Epoxide resins
Scotchpack	3M	Polyester film
Selar	Du Pont	Ethylene-vinyl alcohol copolymers
Sicralan	Degussa	Silicones
Silbione	Rhone-Poulenc	Silicones
Silastic	Dow	Silicones
Silastomer	Dow	Silicones
Silopren	Bayer	Silicone rubber
Siltemp	G.E.	Silicones
Sirfen	Societa Italiana Resine	Phenol-formaldehyde resin
Sirotherm	ICI	Ampholytic polyelectrolyte
Siretene	Societa Italiana Resine	Polyethylene
Skybond	Monsanto	Polyimide
Solef	Solvay	Poly(vinylidene fluoride)
Solvic	Solvay	Poly(vinyl chloride) and blends
Soreflon	Rhone-Poulenc	Polytetrafluoroethylene
Spanzelle	Courtaulds	Spandex fiber
Sparlux	Solvay	Polycarbonate
Stabar	ICI	Polyarylsulfone, polyaryletherketones
Stylac	Asahi	Acrylonitrile-polybutadiene-styrene graft copolymers
Stylex	Mitsubishi	Styrene homopolymers
Styrodur, Styropor	BASF	Styrene homopolymers
Styrocell	Shell	Polystyrene foam
Styrofoam	Dow	Polystyrene foam
Styrol	Idemitsu	Polystyrene
Styron	Dow	Polystyrene
Sumipex	Sumitomo	Poly(methyl methacrylate)
Suntec	Asahi	Polyethylene (HD, LD)
Supec	G.E.	Polyphenylenesulfide
Superacryl	Dental a.s. (Praha)	Poly (methyl methacrylate) dental resin
Surlyn	Du Pont	Ionomers
Technyl A	Rhone-Poulenc	Nylon-6,6
Technyl C	Rhone-Poulenc	Nylon-6
Tecnoflon	Montecatini	Fluoropolymer
Tecolite	Toshiba	Phenol-formaldehyde resins and molding compounds
Tedlar	Du Pont	Poly(vinyl fluoride)
Tedur	Bayer	Polyphenylenesulfide
Teflon	Du Pont	Polytetrafluoroethylene
Teflon FEP	Du Pont	Tetrafluoroethylene-hexafluoropropylene copolymers
Tenac	Asahi	Acetal homopolymers
Tenite	Eastman Chemical	Polyethylenes (HD, LD, LLD)

(continued)

Trade Name	Company	Type of Polymer
Tenite Acetate	Eastman Chemical	Cellulose acetate
Tenite Butyrate	Eastman Chemical	Cellulose acetate–butyrate
Tenite Propionate	Eastman Chemical	Cellulose acetate–propionate
Tenite PTMT	Eastman Chemical	Poly(tetramethylene terephthalate)
Terlenka	Akzo	Poly(ethylene terephthalate)
Terluran	BASF	Acrylonitrile–polybutadiene–styrene graft copolymers
Terylene	ICI	Poly(ethylene terephthalate)
Texicote	Scott Bader	Poly(vinyl acetate)
Texigels	Scott Bader	Acrylic polyelectrolyte
Texin	Mobay	Polyurethane elastomer
Textolite	G.E.	Silicone resins and molding compounds
Thiokol	Thiokol	Polysulfides
Torlon	Amoco	Polyamide–imide
TPX	ICI	Poly-4-methylpent-1-ene
Trans-4	Phillips	<i>Trans</i> -1,4-polybutadiene
Trevira	Hoechst	Polyester fiber
Triax	Bayer	Polyamide/ABS blend
Tricel	Bayer	Cellulose acetate
Trogamid	Dynamit Nobel	Transparent polyamide
Trolen	Dynamit Nobel	Polyethylene
Trolit F	Dynamit Nobel	Cellulose nitrate
Trolitan	Dynamit Nobel	Phenol–formaldehyde resin
Trolitul	Dynamit Nobel	Polystyrene
Trosiplast	Dynamit Nobel	Poly(vinyl chloride) and blends
Trovidur	Dynamit Nobel	Polypropylene, poly(vinylchloride)
Trymer	American Micro	Polyisocyanurate rigid foam
Tybrene	Dow	Acrylonitrile–butadiene–styrene terpolymer
Tynex	Du Pont	Nylon-6,6
Tyrl	Dow	Styrene–acrylonitrile copolymer
Udel	Union Carbide	Polysulfone
Uitem	G.E.	Polyetherimide
Ultradur	BASF	Poly(butylenes terephthalate)
Ultradur A	BASF	Poly(ethylene terephthalate)
Ultraform	BASF	Acetal homopolymer
Ultramid	BASF	Transparent polyamide, copolyamides
Ultrapas	Dynamit Nobel	Melamine–formaldehyde resins
Ultrapek	BASF	Polyaryletherketones
Ultrason E	BASF	Polyarylethersulfones
Ultrax	BASF	Liquid crystal polymers
Ultryl	Phillips	Poly(vinyl chloride)
U-Polymer	Unitika	Polyarylate
Urafil	Akzo	Thermoplastic polyurethane elastomers
Urecoll	BASF	Urea–formaldehyde
Urepan	Bayer	Polyurethane
Uthane	Urethanes India	Thermoplastic polyurethane elastomers
Valox	G.E.	Poly(butylenes terephthalate)
Valtec	Himont	Polypropylene
Vandar	Hoechst	Poly(butylene terephthalate)
Vectra	Celanese, Hoechst	Liquid crystal polymers
Vedril	Montedison	Poly(methyl methacrylate)
Versamid	General Mills	Fatty polyamides
Versicol	Allied Colloids	Acrylic polyelectrolyte
Verton	ICI	Polyphenylenesulfide
Vespel	Du Pont	Polyimide

(continued)

Trade Name	Company	Type of Polymer
Vestamid	Chem. Werke Hüls	Nylon-12
Vestamid E	Chem. Werke Hüls	Polyamide elastomers
Vestiform	Chem. Werke Hüls	Poly(methyl methacrylate)
Vestodur	Chem. Werke Hüls	Poly(butylene terephthalate)
Vestolen	Chem. Werke Hüls	Polyethylene (HD, LD)
Vestolen P	Chem. Werke Hüls	Polypropylene
Vestoran	Chem. Werke Hüls	Polyphenyleneether
Vestyron	Chem. Werke Hüls	Polystyrene
Vibrathane	Uniroyal	Polyurethane casting resins
Victrex	ICI	Liquid crystal polymers
Vidyne R	Monsanto	Transparent polyamide
Vinacel	Goodyear	Poly(vinyl chloride)
Vinavil	Montedison	Ethylene–vinyl acetate copolymers
Vinnapas	Wacker Chemie	Ethylene–vinyl acetate copolymers
Vinnol	Wacker Chemie	Poly(vinyl chloride)
Vinovil	Montedison	Chlorinated polyethylene
Vipla, Viplast	EniChem	Poly(vinyl chloride)
Vistalon	Exxon	Ethylene–vinyl acetate copolymers, Ethylene–propylene–diene terpolymer
Vistanex	Exxon	Polyisobutylene
Vithane	Goodyear	Polyurethanes
Viton A	Du Pont	Vinylidene fluoride– hexafluoropropylene copolymer
Viton B	Du Pont	Vinylidene fluoride– hexafluoropropylene– tetrafluoroethylene terpolymer
Vulcaprene	ICI	Polyurethanes
Vulkollan	Bayer	Polyurethanes
Vydyne	Monsanto	Polyamide resin
Vyrene	U.S. Rubber	Spandex fiber
Welvic	ICI	Poly(vinyl chloride)
Wofatit	VEB Farbenfabrik	Ion-exchange resins
Xydar	Dartco Mfg.	Wholly aromatic copolyester injection- molding resin
Zeo-karb	Permutit Co.	Ion-exchange resins
Zetabon, Zimek	Dow	Ethylene–vinyl acetate copolymers
Zetafin	Dow	Ethylene–methyl acrylate copolymers
Zytel	Du Pont	Nylon-6, nylon-6,6

This selection confers no priorities and is not exhaustive.

A2

Commonly Used Abbreviations for Industrial Polymers

AAS	Copolymer of acrylonitrile, acrylate, and styrene
ABR	Acrylate–butadiene rubber
ABS	Acrylonitrile–butadiene–styrene terpolymer
ACS	Thermoplastic blend of a copolymer from acrylonitrile and styrene with chlorinated polyethylene
AES	Thermoplastic quaterpolymer from acrylonitrile, ethylene, propylene, and styrene
ASA	Copolymer of acrylonitrile, styrene, and acrylates
BR	Butadiene rubber
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate propionate
CMC	Carboxymethyl cellulose
CN	Cellulose nitrate
CPE	Chlorinated polyethylene
CPVC	Chlorinated poly(vinyl chloride)
CR	Polychloroprene
CTA	Cellulose triacetate
CTFE	Chlorotrifluoroethylene polymer
EC	Ethyl cellulose
ECTFE	Ethylene–chlorotrifluoroethylene copolymer
EEA	Elastomeric copolymer from ethylene and ethyl acrylate
EMA	Ethylene–methyl acrylate copolymer
EP	Epoxy resin
E/P	Ethylene–propylene copolymer
EPDM	Terpolymer from ethylene, propylene, and a (nonconjugated) diene
EPM	Ethylene–propylene copolymer
EPR	Elastomeric copolymer of ethylene and propylene
EPT, EPTR	Elastomeric copolymer of ethylene, propylene, and a diene
ETFE	Ethylene–tetrafluoroethylene copolymer
EVA	Copolymer from ethylene and vinyl acetate
EVOH	Ethylene–vinyl alcohol copolymer
FEP	Fluorinated ethylene–propylene copolymer
HDPE	High-density polyethylene
HIPS	High-impact polystyrene
IIR	Butyl rubber (isobutylene–isoprene copolymer)

IPN	Interpenetrating polymer network
IR	Synthetic <i>cis</i> -1,4-polyisoprene rubber
LCP	Liquid crystal polymer
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MBS	Methacrylate–butadiene–styrene copolymer
MF	Melamine–formaldehyde resin
NBR	Acrylonitrile–butadiene rubber (nitrile rubber)
NC	Nitrocellulose (cellulose nitrate)
NR	Natural rubber
PA	Polyamide
PAA	Poly(acrylic acid)
PAE	Polyarylether
PAEK	Polyaryletherketone
PAES	Polyarylethersulfone
PAI	Polyamide–imide
PAMS	Poly- α -methylstyrene
PAN	Polyacrylonitrile
PAr	Polyarylate
PAS	Polyarylsulfide
PB	Polybutadiene
PBT	Poly(butylene terephthalate)
PC	Polycarbonate
PCTG	Poly(cyclohexane terephthalate-glycol)
PDMS	Polydimethylsiloxane
PE	Polyethylene
PEBA	Polyether-block amide
PEC	Polyestercarbonate
PEEK	Polyetheretherketone
PEG	Polyethylene glycol
PEI	Polyetherimide
PEO	Poly(ethylene oxide)
PES	Polyethersulfone
PET	Poly(ethylene terephthalate)
PF	Phenol–formaldehyde resin
PFEP	Copolymer from tetrafluoroethylene and hexafluoropropylene
PI	Polyimide
PIB	Polyisobutylene
PIR	Polyisocyanurate foam
PMMA	Poly(methyl methacrylate)
PO	Polyolefin
POM	Polyoxymethylene (Acetal)
PP	Polypropylene
PPE	Polyphenylether
PPG	Polypropylene glycol
PPO	Poly(phenylene oxide)
PPS	Polyphenylenesulfide
PS	Polystyrene
PSO	Polysulfone
PSU	Polyphenylenesulfone
PTFE	Polytetrafluoroethylene
PTMG	Polyoxytetramethyleneglycol
PTMT	Poly(tetramethylene terephthalate)

PU	Polyurethane
PVA	Poly(vinyl alcohol), Poly(vinyl acetate)
PVAc	Poly(vinyl acetate)
PVAL	Poly(vinyl alcohol)
PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)
PVDC	Poly(vinylidene chloride)
PVDF	Poly(vinylidene fluoride)
PVF	Poly(vinyl fluoride)
PVFM	Poly(vinyl formal)
PVME	Poly(vinyl methyl ether)
PVOH	Poly(vinyl alcohol)
PVP	Poly(vinyl pyridine), Poly(vinyl pyrrolidone)
RTV	Room temperature vulcanizing silicone rubber
SAN	Styrene–acrylonitrile copolymer
SBR	Styrene–butadiene rubber
SBS	Styrene–butadiene–styrene block copolymer
SEBS	Styrene–ethylene–butylene–styrene block copolymer (hydrogenated SIS)
SIN	Simultaneous interpenetrating network
SIS	Styrene–isoprene–styrene block copolymer
SMA	Styrene–maleic anhydride copolymer
SMS	Styrene– α -methylstyrene copolymer
TPE	Thermoplastic elastomer
TPEs	Thermoplastic polyesters, e.g., PBT and PET
TPO	Thermoplastic polyolefin elastomers
TPU	Thermoplastic polyurethane
UF	Urea–formaldehyde resin
UHMWPE	Ultrahigh-molecular weight polyethylene (mol. wt. $> 3 \times 10^6$)
VLDPE	Very-low-density polyethylene (density ca. 0.890–0.915 g/cm ³)

A3

Index of Trade Names, Manufacturers, and Suppliers of Antioxidants

The following index of trade names, manufacturers, and suppliers is based on a choice of representative antioxidants for thermoplastics. No claim is made for completeness. Detailed lists can be found in the source cited.

The letters A to M symbolize chemical classes of compounds with the following meanings: A=alkylphenols; B=alkylidene-bisphenols (molecular weight 300–600); C=alkylidene-bisphenols (molecular weight >600); D=thiobisphenols (molecular weight 300–600); E=hydroxybenzyl compounds (molecular weight 300–600); F=hydroxy-benzyl compounds (molecular weight >600); G=Acylaminophenols (4-hydroxyanilides); H=octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate; I=poly-hydroxyphenylpropionates (molecular weight >600); J=amines; K=thioethers; L=phosphites and phosphonites; M=zinc dibutyldithiocarbamate.

Trade Name	Chemical Class													Manufacturer/Supplier
	A	B	C	D	E	F	G	H	I	J	K	L	M	
Age Rite										X			X	R.T Vanderbilt Norwalk, CT, U.S.A.
Vanox		X				X			X	X	X	X		Ente Nazionale Idrocarburi, Rome, Italy
Anox	X							X	X	X				
CAO	X	X		X										Ashland Chemical Ltd., Columbus, OH, U.S.A.
Carstab									X	X				Morten Thiokol Inc., Danvers, MA, U.S.A.
Cyanox		X				X					X			American Cyanamid Co., Wayne, NJ, U.S.A.
Ethanox		X		X		X		X						Ethyl Corporation, Baton Rouge, LA, U.S.A.
Good-rite						X			X	X				B.F. Goodrich Chemical Group, Cleveland, OH, U.S.A.
Hostanox			X								X	X		Hoechst AG, Frankfurt, Germany; American Hoechst Corp., Somerville, NJ, U.S.A.

(continued)

Trade Name	Chemical Class													Manufacturer/Supplier
	A	B	C	D	E	F	G	H	I	J	K	L	M	
HPM			X											Societe Francaise d'Organo-Synthese, Neville-sur-seine, France
Garbexif Ionol	X	X		X							X	X		Shell Nederland Chemie BV, Gravenhage, Netherlands
Ionox Irgafos						X						X		Ciba-Geigy AG, Basel, Switzerland; Ciba-Geigy Corp., Hawthorne, NY, U.S.A.
Irganox Isonox	X	X		X	X	X	X	X	X	X	X			Schenectady Chemicals Inc., Schenectady, NY, U.S.A.
Keminox	X	X	X	X		X								Chemipro Kasei Ltd., Chuo-Ka, Kobe, Japan
Lowinox	X	X		X				X	X	X	X	X		Chemische Werke Lowi GmbH, Waldkraiburg, Germany
Mark										X		X		Argus Chemical S.A.-N.V., Brussels, Belgium; Witco Chem. Co., New York, NY, U.S.A.
Mixxim		X										X		Fairmount Chem. Co., Newark, NJ, U.S.A.
Naugard		X	X					X	X	X	X	X	X	Uniroyal Ltd., Bromsgrove, Worcs., U.K.; Uniroyal
Naugawhite Polygard		X										X		Chem., Naugatuck, CT, U.S.A.
Nonox	X	X								X				ICI Ltd., London, U.K.
Topanol	X	X								X				ICI Americas, Wilmington, DE, U.S.A.
Negonox Oxi-chek		X	X					X						Ferro Corp. Chem. Div., Walton Hills, OH, U.S.A.
Perkanox	X													Akzo Chemie, Nederland NV, Amsterdam, Netherlands
Permanax	X	X												Vulanax International, Saint Cloud, France
Samilizer		X		X				X	X		X	X		Sumitomo Chemical Co. Ltd., Osaka, Japan
Antigene Santonox				X						X				Monsanto Europe SA., Brussels, Belgium; Monsanto Co., Akron., OH, U.S.A.
Santowhite Santoflex	X	X		X						X				
Santicizer Seenox			X	X		X						X		
Tominox								X	X					Shipro Kasei Ltd., Kita-ku, Osaka, Japan
Yoshinox Vulkanox	X	X		X						X	X			Yoshitomi Pharmaceutical Ind. Ltd., Osaka, Japan
Weston												X		Mobay Chem. Corp., Pittsburgh, PA, U.S.A.
														Borg-Warner Chemicals., Parkersburg, WV, U.S.A.

(continued)

Trade Name	Chemical Class														Manufacturer/Supplier
	A	B	C	D	E	F	G	H	I	J	K	L	M		
Ultranox	X	X		X				X		X		X		Goodyear SA, Rueil-Malmaison, France; Goodyear, Atkron, OH, U.S.A.	
Wing Stay	X			X						X					
Wytox	X	X								X		X		Otlin Corp., Stamford, CT, U.S.A.	

Source: Henman, T. J. 1982. *World Index of Polyolefin Stabilizers*, Kogan Page, London.

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Index of Trade Names, Manufacturers, and Suppliers of Metal Deactivators

Trade Name	Chemical Class	Manufacturer/Supplier
Cyanox	Not disclosed	Cyanamid GmbH, Wolfratschausen, Germany American Cyanamid Co., Wayne, NJ, U.S.A.
Eastman Inhibitor OABH	Dibenzalhydrazone	Eastman Chemical Products, Kingsport, TN, U.S.A.
Hostanox	Phosphorous acid ester	Hoechst AG, Augsburg, Germany
Irganox MD	Diacylhydrazine	Ciba-Geigy AG, Division KA, Basel, Switzerland Ciba-Geigy Crop., Plastics and Additives Div., Hawthorne, NY, U.S.A.
Mark	Not disclosed	Argus Chemical SA, Drogenbos, Belgium Argus Chemical Corp., Brooklyn, NY, U.S.A.
Naugard	Oxalamide derivative	Uniroyal Chemical, Naugatuck, CT, U.S.A.

Source: Henman, T. J. 1982. *World Index of Polyolefin Subilizers*, Kogan Page Ltd., London.

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Index of Trade Names, Manufacturers, and Suppliers of Light Stabilizers

The following index of trade names, manufacturers, and suppliers is based on a choice of representative light stabilizers for thermoplastics. No claim is made for completeness. Detailed lists can be found in the source cited.

The letters A to J symbolize chemical classes of compounds with the following meanings: A=benzophenones; B=benzotriazoles; C=nickel compounds; D=salicylates; E=cyanocinnamates; F=benzylidene malonates; G=benzoates; H=oxanilides; I=sterically hindered amies and J=polymeric sterically hindered amines.

Trade Name	Compound Type	Manufacturer
Aduvex	A	Ward Blenkinsop and Co. Ltd., Wembley (Middx.),
Anti-UV	A, D	Societe Francaise D'Organo Synthese. Neuilly-sur-Seine, France
Carstab	A	Cincinnati Milacron Chemicals Inc., New Brunswick, NY, U.S.A.
Chimassorb	A, C, J	Chimosa S.p.A., Pontecchio Marconi, Italy
Cyasorb UV	A, B, C, E, F, I, J	American Cyanamid Co., Wayne, NJ, U.S.A.
Eastman Inhibitor	A	Eastman Chemical Product Inc. Kingsport, TN, U.S.A.
UV-Chek AM	A, C, G	Ferro Corp., Cleveland, OH, U.S.A.
Goodrite UV	I	B. F. Goodrich, Chemical Group, Cleveland, OH, U.S.A.
Hostavin	A, I, K	Hoechst AG, Frankfurt/M. Germany
Interstab	G	Interstab Ltd., Liverpool, U.K.
Irgastab	C	Ciba-Geigy AG, Basel Switzerland
Mark	A, I	Argus Chemical Corp., Brooklyn, NY, U.S.A.
Mixxim	I, J	Fairmount Chemical Co., Newark, NJ, U.S.A.
Rylex	A, C	E. I. Du Pont de Nemours and Co., Wilmington, DE, U.S.A.
Salol	A, D	Dow Chemical Co., Midland, MI, U.S.A.
Sanol LS	I	Sankyo Co. Ltd., Tokyo, Japan
Seesorb	A, B, C, D, E, G	Sun Chemical Corp., Tokyo, Japan
Sumisorb	A, D	Sumitomo Chemical Co., Ltd., Osaka, Japan
Tinuvin	B, H, I, J	Ciba-Geigy AG, Basel, Switzerland
UV-Absorber Bayer	A, E	Bayer AG, Leverkusen, Germany
Uvinul	A, E	BASF AG, Ludwigshafen, Germany
Viosorb	A, B, D	Kyodo Chemical Co. Ltd., Tokyo, Japan

Source: Henman, T. J. 1982. *World Index of Polyolefin Stabilizers*, Kogan Page Ltd., London.

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Index of Trade Names and Suppliers of Flame Retardants

The following index of trade names and suppliers is based on a choice of representative flame retardants for thermoplastics. No claim is made for completeness. Detailed lists can be found in the source cited.

Trademark	Chemical Class	Producer
Amgard	Phosphoric acid ester	Albright and Wilson, London, U.K.
Chlorowax	Chlorinated paraffins	Diamond Shamrock Plastics Div., Cleveland OH, U.S.A.
Cereclor	Chlorinated paraffins	ICI, London, U.K.
Dechlorane	Chlorine containing cycloaliphatics	Occidental Chemical Corp., Niagara Falls, NY, U.S.A.
Disflamoll	Organic phosphates and halogenated organic phosphates	Bayer AG, Leverkusen, Germany
Exolit	Chlorinated paraffins, organic phosphates	Hoechst AG, Frankfurt/M, Germany
Firebrake	Inorganic flame retardants	US Borax & Chem. Corp., Los Angeles, CA, U.S.A.
Fire Fighters	Organic bromine compounds	Great Lakes Chem. Corp., West Lafayette, IN, U.S.A.
Fireguard	Organic bromine compounds	Teijin Chem. Co., Nishishinbasi, Tokyo, Japan
Firemaster	Organic bromine compounds	Great Lakes Chem. Corp., West Lafayette, IN, U.S.A.
Fire-Shield	Organic bromine compounds, antimony trioxide	PPG Industries Inc., Chicago, IL, U.S.A.
Firex	Organic halogenated compound with antimony trioxide	Dr. Th. Bohme KG. Geretstried, Germany
Flammastik	Flame retardant on the basis of antimony	Chem. Fabrik Grunau GmbH, Illertissen, Germany
Hydral	Hydrated alumina	Aluminum Company of America, Pittsburgh, PA, U.S.A.
Ixol	Organic bromine and chlorine compounds	Kali-Chemie AG, Hannover, Germany
Martinal	Hydrated alumina	Martinswerk GmbH, Bergheim, Germany
Nonnen	Organic bromine compounds	Marubeni Corp., Osaka, Japan
Nyacol	Flame retardant on the basis of antimony	Nyacol Products Inc., Ashland, MA, U.S.A.
Phosflex	Organic phosphates	Stauffer Chem. Co., Specialty Chem. Div., Westport, CT, U.S.A.
Proban	Phosphoric acid esters, quaternary phosphonium compounds	Albright and Wilson, London, U.K.
Pyro-Check	Organic bromine compounds	Ferro Corp., Chem. Div., Bedford, OH, U.S.A.
Pyrovatex	Organic phosphates	Ciba-Geigy AG, Basel, Switzerland

(continued)

Trademark	Chemical Class	Producer
Sandoflam	Flame retardants based on organic bromine compounds	Sandoz AG, Basel, Switzerland
Santicizer	Phosphoric acid esters, halogenated organic compounds	Monsanto Co., St. Louis, MO, U.S.A.
Saytex	Organic bromine compounds	Ethyl Corp., Chemical Group, Baton Rouge, LA, U.S.A.
Tardex	Organic bromine compounds	ISC-Chemicals, Avonmouth, Bristol, England
Timonox	Antimony oxides	Cookson Ltd., Stoke-on-Trent, England
Zerogen	Hydrated alumina	Solem Industries, Inc., Norcross, GA, U.S.A.
—	Smoke reducer based on molybdenum	Climax Molybdenum Co. Ltd., London, U.K.

Source: Troitzsch, J. 1983. *International Plastics Flammability Handbook*, Carl Hanser Verlag, Munchen.

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Index of Trade Names and Suppliers of Foaming Agents

The following index of trade names and suppliers is based on a choice of representative foaming agents for thermoplastics. No claim is made for completeness. Detailed lists can be found in the source cited.

Chemical Foaming Agent	Trade Name and Supplier ^a	Processing Temperature Range, (°C)	Gas Yield (cm ³ /g)	Recommended for
Azodicarbonamide (1,1'-azobisformamide)	Azofoam (Biddle Sawyer); Porofor (Miles); Kempore (Uniroyal); Ficel AC (Schering); Plastifoam (Plastics & Chem.); Cellcom (Plastics & Chem.); Unicell D (Dong Jin)	150–230	220	ABS, Acetal, Acrylic, EVA, HDPE, LDPE, PPO, PP, PS, HIPS, flexible PVC, TPE
Modified azodicarbonamide (rigid PVC grade)	Kempore (Uniroyal); Plastifoam (Plastics & Chem.); Celogen AZRV (Uniroyal); Unicel DXRV (Dong Jin); Azofoam DS-1, DS-2 (Biddle Sawyer); Ficel AC2 (Schering)	150–200	155–230	PP, rigid PVC
Modified azodicarbonamide (flexible PVC open cell grade)	Azofoam F (Biddle Sawyer)	200–230	80–90	Flexible PVC
Dinitroso pentamethylene-tetramine	Opex 80 (Uniroyal); DNPT (Dong Jin); Mikrofine SSS (High Polymer Labs); Unicel GP9, GP3, GP42 (Dong Jin)	125–190	240	ABS, polyurethane, silicone, natural rubber, SBR

(continued)

Chemical Foaming Agent	Trade Name and Supplier ^a	Processing Temperature Range, (°C)	Gas Yield (cm ³ /g)	Recommended for
4,4'-Oxybis (benzenesulfonyl) hydrazine	Cellcom OBSH-ASA2 (Plastics & Chem); Celogen OT (Uniroyal); Azofoam B-95 (Biddle Sawyer); Unicell OH (Dong Jin); Azocel OBSH (Fairmount); Mikrofine OBSH (High Polymer Labs)	120–190	120–125	EVA, LDPE, PS, flexible PVC
5-Phenyltetrazole	Expandex 5PT (Uniroyal); Unicell 5PT (Dong Jin); Plastifoam (Plastics & Chem.)	230–290	200	PFO, TPEs, PC, polysulfone, nylon, polyetherimide
<i>p</i> -Toluenesulfonyl semicarbazide	Unicell TS (Dong Jin); Celogen RA (Uniroyal); Mikrofine TSSC (High Polymer Labs)	200–235	145	ABS, Acetal, Acrylic, EVA, HDPE, LDPE, PFO, PP, PS, HIPS, PVC, TPE
2,2'-Azobisisobutyronitrile	Mikrofine AZDM (High Polymer Labs)	90–115	125	Silicone rubber, semirigid PVC

^aNames and addresses as follows: Biddle Sawyer Corp., 2 Penn Plaza, New York, NY 10121; Dong Jin (U.S.A.) Inc., 38 W. 32 St., Suite 902, New York, NY 10001; Fairmount Chemical Co., 117 Blanchard St., Newark, NJ 07105; High Polymer Labs, 803, Vishal Bhawan, 95 Nehru Place, New Delhi 110019, India; Miles Inc., 2603 W. Market St., Akron, OH 44313; Plastics & Chemicals Inc., P.O. Box 306, Cedar Grove, NJ 07009; Schering Berlin Polymers, 4868 Blazer Memorial Pkwy, Dublin, OH 43017; Uniroyal Chemical Co., World Headquarters, Middlebury, CT 06749.

Source: *Modern Plastics*, Mid-November 1994, p. C-73.

A8

Harmonic Motion of a Maxwell Model

Trigonometric Notation

Starting with a sinusoidal input of strain in a Maxwell element (see [Chapter 3](#)), we derive the resulting sinusoidal stress. First we let the strain ϵ be a function of a maximum or peak strain ϵ_0 and time t with a frequency ω :

$$\epsilon = \epsilon_0 \sin \omega t \quad (\text{A8.1})$$

For the Maxwell element:

$$\frac{d\epsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\lambda E} \quad (\text{A8.2})$$

Differentiating Equation A8.1:

$$\frac{d\epsilon}{dt} = \omega \epsilon_0 \cos \omega t \quad (\text{A8.3})$$

Rearranging Equation A8.2:

$$\frac{d\sigma}{dt} + \frac{\sigma}{\lambda} = \omega \epsilon_0 E \cos \omega t \quad (\text{A8.4})$$

This is a simple linear differential equation of the form

$$\frac{dy}{dx} + Py = Q$$

The general solution for such an equation, when P and Q are functions of x only, is

$$y \exp(\psi) = \int \exp(\psi) Q dx + C, \quad \psi = \int P dx \quad (\text{A8.5})$$

For Equation A8.4, the analogy is

$$\psi = \frac{t}{\lambda} \quad (\text{A8.6})$$

$$\sigma \exp\left(\frac{t}{\lambda}\right) = \omega \epsilon_0 E \int \exp\left(\frac{t}{\lambda}\right) \cos \omega t \, dt + C \quad (\text{A8.7})$$

$$\sigma \exp\left(\frac{t}{\lambda}\right) = \frac{\omega \epsilon_0 E \lambda}{1 + \omega^2 \lambda^2} (\cos \omega t + \omega \lambda \sin \omega t) \exp\left(\frac{t}{\lambda}\right) + C \quad (\text{A8.8})$$

or

$$\sigma = \frac{\omega \lambda}{1 + \omega^2 \lambda^2} \epsilon_0 E (\cos \omega t + \omega \lambda \sin \omega t) + C \exp\left(\frac{-t}{\lambda}\right) \quad (\text{A8.9})$$

The second term on the right is a transient one which drops out in the desired steady-state solution for $t/\lambda \gg 1$.

Let us now define an angle δ by

$$\tan \delta = \frac{1}{\omega \lambda} = \frac{\sin \delta}{\cos \delta} \text{ and } \sin \delta = \frac{1}{(1 + \omega^2 \lambda^2)^{1/2}} \quad (\text{A8.10})$$

Then, making use of trigonometric identities:

$$\cos \omega t + \omega \lambda \sin \omega t = \frac{\cos \omega t (\sin \delta)}{\sin \delta} + \frac{\sin \omega t (\cos \delta)}{\sin \delta} \quad (\text{A8.11})$$

$$= \frac{\sin(\omega t + \delta)}{\sin \delta} \quad (\text{A8.12})$$

$$= (1 + \omega^2 \lambda^2)^{1/2} \sin(\omega t + \delta) \quad (\text{A8.13})$$

Finally, combining Equation. A8.13 and Equation A8.9 with the transient term dropped, one arrives at

$$\sigma = \frac{\omega \lambda}{(1 + \omega^2 \lambda^2)^{1/2}} \epsilon_0 E \sin(\omega t + \delta) \quad (\text{A8.14})$$

Complex Notation

Starting with a complex strain, the real part of which is the actual strain:

$$\epsilon^* = \epsilon_0 \exp(i\omega t) \quad (\text{A8.15})$$

The motion of the Maxwell element, in terms of a complex stress and strain, is

$$\frac{d\epsilon^*}{dt} = \frac{1}{E} \frac{d\sigma^*}{dt} + \frac{\sigma^*}{\lambda E} \quad (\text{A8.16})$$

Differentiating Equation A8.15:

$$\frac{d\epsilon^*}{dt} = i\omega \epsilon_0 \exp(i\omega t) \quad (\text{A8.17})$$

Rearranging Equation A8.16 and Equation A8.17:

$$\frac{d\sigma^*}{dt} + \frac{\sigma^*}{\lambda} = E \frac{d\epsilon^*}{dt} = i\omega\epsilon_0 E \exp(i\omega t) = Q \quad (\text{A8.18})$$

As in Equation A8.5, the general solution is

$$\sigma^* \exp\left(\frac{t}{\lambda}\right) = \int \exp\left(\frac{t}{\lambda}\right) Q dt + C \quad (\text{A8.19})$$

$$\begin{aligned} \int \exp\left(\frac{t}{\lambda}\right) Q dt &= i\omega\epsilon_0 E \int \exp(i\omega t + \frac{t}{\lambda}) dt \\ &= \frac{i\omega\epsilon_0 E \exp(i\omega t + t/\lambda)}{i\omega + 1/\lambda} \end{aligned} \quad (\text{A8.20})$$

Substitution and rearrangement yields

$$\sigma^* = \frac{i\omega\epsilon_0 \lambda E \exp(i\omega t)}{i\omega\lambda + 1} + C \exp\left(-\frac{t}{\lambda}\right) \quad (\text{A8.21})$$

Once again, the second term on the right-hand side is a transient term that drops out at $t/\lambda \gg 1$. Multiplying both numerator and denominator by $1 - i\omega\lambda$ and substituting ϵ^* for its equivalent, $\epsilon_0 \exp(i\omega t)$ gives

$$\sigma^* = \frac{\omega^2 \lambda^2 \epsilon^* E + i\omega \lambda \epsilon^* E}{1 + \omega^2 \lambda^2} \quad (\text{A3.22})$$

Rearranging gives

$$\frac{\sigma^*}{\epsilon^*} = \frac{E\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} + \frac{i(E\omega \lambda)}{1 + \omega^2 \lambda^2} \quad (\text{A3.23})$$

The definition of complex E^* is

$$E^* = E' + iE'' = \frac{\sigma^*}{\epsilon^*} \quad (\text{A3.24})$$

Comparing Equation A8.23 and Equation A8.24 one concludes that

$$E' = \frac{E\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \text{ and } E'' = \frac{E\omega \lambda}{1 + \omega^2 \lambda^2} \quad (\text{A3.25})$$

The dynamic modulus E' , which is the real component of E^* , is associated with energy storage and release in the periodic deformation and is therefore called the storage modulus. The imaginary part of the modulus, E'' , is associated with viscous energy dissipation and is called the loss modulus (see [Chapter 3](#) for more details).

A9

Formulations of Flame-Retarded Selected Thermoplastics

In the following formulations the fire performance properties of flame-retarded thermoplastics are compared with those of the base resin, the properties of the latter being given in brackets. The test methods used are: ASTM-D 633-77, the value for average time of burning (ATB) given in seconds and that for average extent of burning (AEB) in millimeters; ASTM 2863-77, limiting oxygen index (LOI) in % O₂.

Low-Density Polyethylene (LDPE)

90.5%	LDPE
6.0%	Chlorinated paraffin (70% chlorine)
3.5%	Antimony trioxide

Properties

ASTM	ATB	<5	(160)
	AEB	18	(100)
	LOI	23.75	(17.5)

High-Density Polyethylene (HDPE)

89.9%	HDPE
5.0%	Octabromodiphenyl
1.6%	Chlorinated paraffin (70% chlorine)
3.5%	Antimony trioxide

Properties

ASTM	ATB	<5	(210)
	AEB	20	(100)
	LOI	25.75	(16.75)

Polypropylene

94.5%	Polypropylene
3.5%	Bis-dibromopropylether of tetrabromobisphenol A
2.0%	Antimony trioxide

Properties

ASTM	ATB	5	(195)
	AEB	14	(100)
	LOI	27.5	(18.25)

Polystyrene

a.	<i>Crystal Polystyrene</i>
97%	Polystyrene
3%	Hexabromocyclododecane

Properties

ASTM-D635	ATB	<5	(117)
	AEB	28	(100)

b.	<i>Impact Polystyrene</i>
80%	Impact polystyrene
15%	Octabromodiphenyl
5%	Antimony trioxide

Properties

ASTM	ATB	<5	(150)
	AEB	17	(100)
	LOI	25.0	(16.5)

c.	<i>Polystyrene Foam</i>
82%	Polystyrene
13%	Decabromodiphenyl ether
5%	Antimony trioxide

Properties

ASTM	ATB	<5	(90)
	AEB	19	(100)

Plasticized PVC

53.5%	Suspension PVC
27.7%	Diethylphthalate
4.9%	Epoxidized oleic acid ester
4.9%	Pentabromodiphenyl ether
8.3%	Tricresyl phosphate
0.5%	Lubricant
0.4%	Stabilizer (butyltin carboxylate)

[The formulation passes the FMVSS 302 (Federal Motor Vehicle Safety Standard) test used for the assessment of the burning behavior of materials used for vehicle interiors. A specimen of $35.5 \times 10.0 \times$ max. 13 cm is mounted horizontally and ignited for 15 sec. The rate of flame spread should not exceed 10 cm/min.]

ABS Terpolymer

82%	ABS
13%	Octabromodiphenyl ether
5%	Antimony trioxide

Properties

ASTM	ATB	<5	(195)
	AEB	10	(100)
	LOI	24	(18)

Saturated Polyester

a. Polyester

88%	Poly (butylene terephthalate) (PBTP)
8%	Octabromodiphenyl
4%	Antimony trioxide

Properties

ASTM	ATB	<5	(240)
	AEB	16	(100)
	LOI	28.5	(22.0)

b. Polyester with Glass Fiber Reinforcement

87%	PBTP (30% glass fiber)
9%	Decabromodiphenyl
4%	Antimony trioxide

Properties

LOI	33	(19)
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Polycarbonates

Flame-retarded polycarbonates preferably contain tetrabromobisphenol-A as flame-retardant added before polycondensation. Untreated polycarbonate can be processed to a flame-retardant product as follows:

93.1%	Polycarbonate
5.0%	Decabromodiphenyl ether
1.9%	Antimony trioxide

Properties

ASTM	ATB	< 5	(17)
	AEB	12	(24)
	LOI	40	(25)

Polyamidesa. *Nylon-6*

84%	Nylon-6
10%	Decabromodiphenyl ether
6%	Antimony trioxide

Properties

ASTM	ATB	< 5	(178)
	AEB	17	(60)
	LOI	22.75	(21.75)

b. *Fiberglass-Reinforced Nylon-6*

53%	Nylon-6
22%	Fiberglass
18%	Dechlorane 602
7%	Antimony trioxide

Properties

LOI	32	(21)
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Formulations of Selected Rubber Compounds

Representative formulations (in parts by weight) of several rubber compounds and their normal curing conditions are given below.

Tread Compound for Passenger Tires

Smoked sheet	50
SBR 1712	70
Zinc oxide	5
Stearic acid	2
ISAF black	60
Softener	2
Antioxidant (diphenylamine-acetone condensate)	1.5
Accelerator (CBS)	1
Sulfur	2.2

Cure: 40 min. at 150°C.

Sidewall Compound for Passenger Tires

Smoked sheet	50
SBR 1712	70
Zinc oxide	5
Stearic acid	2
HAF black	45
Softener	2
Antioxidant (diphenylamine-acetone condensate)	1.5
Accelerator (CBS)	1
Sulfur	2.2

Cure: 30 min. at 150°C.

Tube Compound for Car Tires

Butyl (Polysar 301)	100
<i>p</i> -Dinitroso benzene (Polyac)	0.15
FEF black	60
Mineral oil (butyl grade)	20
Zinc oxide	5
Stearic acid	2

(continued)

Accelerators	
MBT	1
TMT	1
Sulfur	1.5

Cure: 30 min. at 160°C.

Friction Compound for Conveyor Belts

Smoked sheet	100
Zinc oxide	5
Stearic acid	2
SRF black	10
Whiting/activated calcium carbonate	15
Tackifier/softener	5
Antioxidant	1
Accelerator (CBS)	0.6
Sulfur	2.5

Cure: 20 min. at 150°C.

Cover Compound for Conveyor Belts

Smoked sheet	50
SBR 1500	50
Zinc oxide	5
Stearic acid	2
Tackifier/softener	5
ISAF black	40
Antioxidant	1.5
Accelerator (CBS)	1.0
Sulfur	2.0

Cure: 20 min at 150°C.

Insulation Compound for Cables

Smoked sheet	100
Zinc oxide	20
China clay	30
Precipitated calcium carbonate	45
Paraffin wax	2
Stearic acid	0.5
Antioxidants	1.0
Accelerators	
DPG	0.5
MBTS	1.0
Sulfur	1.5

Cure: 15 min at 140°C.

Translucent Shoe Soling Compound

Pale crepe	100
Zinc oxide	3
Stearic acid	1
Precipitated silica	50
Paraffin wax	1

(continued)

Spindle oil	2
Diethylene glycol	2
Antioxidant (styrenated phenol)	1
Accelerators	
TMTM	0.5
ZDC	0.75
Sulfur	2.5

Cure: 7 min at 150°C.

Microcellular Shoe Soling

Smoked sheet	20
SBR 1500	20
SBR 1958	60
Peptizer	1
Microcellular crumb	60
Zinc oxide	5
Stearic acid	3–5
Paraffin wax	1
Mineral oil	10
Coumarone-indene resin	5
Styrenated phenol	1
Aluminum silicate	40
China clay	100
Blowing agent (DNPT)	5
Accelerators	
DPG	0.5
MBTS	1.0
Sulfur	2.5

Cure: 8 min at 150°C; oven stabilization at 100°C, 4 h.

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Formulations of Selected PVC Compounds

The formulations given below (in parts by weight) are example of typical formulations of PVC compounds from the many available, which have been designed to meet specific requirement of different applications.

Glass-Clear Food Packaging Film

PVC	100
Octyltin mercaptide	1–1.5
Glycerol ester	0.5–1.0
Ester wax	0.1–0.4

Furniture Film

PVC	100
Plasticizer	15–25
Epoxidized soybean oil	2–3
Liquid Ba/Cd stabilizer	1.5–2.0
UV absorber	0.2–0.4
Bis-amide wax	0.2–0.4
Processing aid	1
Pigment	0.5–10.0

Flexible Film for Outdoor Application

PVC	100
Plasticizer	40–80
Epoxy plasticizer	2–3
Tin carboxylate stabilizer	1–2.5
UV absorber	0.2–0.5
Oxidized polyethylene wax	0.2–0.4

Transparent Sheet for exterior Application

PVC	100
Butyltin mercaptide	2–2.5
Fatty alcohol	0.5–0.8
Fatty acid ester	0.5–0.8

(continued)

Polyethylene wax	0.1–0.2
Processing aid	1–2
UV absorber (benzotriazole type)	0.3–0.5

Artificial Leather Cloth

Base coat	
PVC	100
Plasticizer	50–100
Epoxidized soybean oil	2–3
Barium/zinc stabilizer	1.5–2.0
Filler	0–20
Top coat	
PVC	100
Plasticizer	40–60
Epoxidized soybean oil	3–5
Barium/zinc stabilizer	1.5–2.0
UV absorber	0.2–0.3

Bottles for Food Packaging

PVC	100
Processing aid	0.5–1.0
Methyl- or octyltin mercaptide	1.0–1.5
Lubricant	0.5–1.5
Impact modifier	5–10

Potable Water Pipes

PVC	100
Methyltin mercaptide, ^a octyltin mercaptide, ^a butyltin mercaptide ^a	0.3–0.4
Calcium stearate	0.5–0.8
Solid paraffin wax	0.6–0.8
Polyethylene wax	0.1–0.2

In compliance with specific national regulations.

Pressure Pipes and Conduits

PVC	100
Tribasic lead sulfate	0.5–1.0
Dibasic stearate	0.5–1.0
Calcium stearate	0.2–0.4
Stearic acid and/or paraffin wax	0.2–0.5

Calendered Floor Tiles

PVC	100
Plasticizer	30–70
Epoxidized soybean oil	2–5
Solid Ba/Cd stabilizer	1.5–2.5
Stearic acid	0.1–0.4
Chalk	50–100

Wire and Cable Insulation

PVC	100
Plasticizer	30–60
Tribasic lead Sulfate	2–4
Normal lead stearate	0.5–1.5
Chalk	20–40
Stearic acid and/or paraffin wax	0–0.2

Windows Profiles

PVC	100
Impact modifier	6–12
Modified tin maleate stabilizer	2–2.5
Paraffin wax	0.6–1.2
Oxidized polyethylene wax	0.6–1.2
Antioxidant	0.1
UV absorber	0.2–0.4
Titanium dioxide	2–4
Chalk	10

Shoe

PVC	100
Plasticizer	50–80
Epoxidized soybean oil	2–3
Liquix Ba/Cd stabilizer	1.5–2.0
Stearic acid	0.2–0.4

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Formulations of Polyurethane Foams

The formulations given below (in parts by weight) are three examples of typical formulations from the many available, which have been designed to meet specific requirements. Noteworthy points reading the formulations are explained. An example of formulation for reaction injection molding (RIM) and reinforced reaction injection molding (RRIM) is also given,

In order to achieve the desired balance of hydroxyl to isocyanate groups in a formulation, the *isocyanate index* is specified:

$$\text{Isocyanate index} = \frac{\text{Number of mole equivalents of isocyanate}}{\text{Number of mole equivalents of polyols}} \times 100$$

If water is included in the formulation, this is also included in the mole equivalent of polyol.

A Typical Rigid Foam Formulation

Component A		
Polyol mixture containing a significant amount of triols and hex/octols to produce cross-linking		100
Catalyst 1	<i>N,N</i> -cyclohexylamine	0.3
Catalyst 2	<i>N,N</i> -dimethylethanolamine	0.3
Freon 11	(CFCI ₃)	50
Water		1
Surfactant	(A block copolymer of polyether and silicone)	1
Component B		
Impure liquid MDI	Equal in volume to component A and to give an isocyanate index near to 100	

Notes on Formulation A

1. In the formulation of the foam, the equipment perform better with approximately equal volumes of components A and B.
2. The MDI is of functionality around 2.2. This functionality together with aromatic nature of the MDI will tend to give rigid foams.
3. The isocyanate index is quoted as 100 to give conditions essentially producing urethane and urea group only.
4. Freon 11 blows to give closed cell structures whereas water produces open cells through carbon dioxide. This formulation is typical for a rigid foam for thermal insulation purposes. The heat build-up due to the reaction exotherm (about 80 kJ/mole for formation of urethane groups) is sufficiently dissipated through the open cell to avoid thermal degradation.

5. The catalyst combination allows a balance of reactions since catalyst 2 is specific to the water reaction. The values given are notional and depend on the polyols used.
6. A surfactant is used to stabilize the bubble structure.
7. It is likely that the product foam will have a density of 30 kg/m³ which is roughly composed of 97% gas and 3% matrix by volume.

Formulation B A Typical flexible Foam Formulation

Component A		
Polyether polyol with long chains and overall low functionality		100
Water		4.5
Catalyst 1 (a tertiary amine)		0.15
Catalyst 2 (stannous octoate)		0.2
Freon 11		10
Silicone surfactant		1.3
Component B		
TDI (to index 112)		58.4

Notes on Formulation B

1. This is a standard foam grade formulation. Other flexible foam formulations are available for supersoft, high resilience and special grades.
2. The formulation is designed to give open cells.
3. The isocyanate has functionality of 2.0 and hence will not itself give cross-linking.

Formulation C A Typical flexible Foam Formulation

Component A		
A flame retardant polyol		100
Catalyst 1,	DMP (tris-2,4,6-dimethylamionomethyl phenol)	3
Catalyst 2,	Sodium acetate: potassium acetate (1: 1) 33% w/w in ethane-1,2-diol	2
Freon 11		40
Surfactant	(silicone type)	1.5
Component B		
A liquid isocyanate based on MDI (to give index 200)		142.6

Notes On Formulation C

1. The high isocyanate index of catalyst system will promote the formation of isocyanate structures.
2. The higher heat stability of the isocyanate structures will be enhanced by a fire-retardant grade of polyol.

Formulation D A Typical RIM/RRIM Formulation

Component A		
Polyol mixture	Overall functionality 2.5, and containing primary hydroxyl terminated polyethers	100
Diol hardener	(1,4-Butanediol)	5
Soluble	(Soluble tin salt)	2

(continued)

Surfactant		1
Blowing agent	Freon 11	5
Milled glass fiber	(For RRIM)	5–30% of total
Component B		
Modified isocyanate based upon MDI		To match index 95–110

A Note on RIM and RRIM

RIM and RRIM require that a liquid isocyanate compound (component B) is effectively mixed with another liquid (component A) which contains polyols, catalysts, and other agents. Components A and B are metered and pumped into mixing heads where the two immiscible components are each turbulently broken down into small droplets surrounded by the other component phase. (The nozzles on the mixing head are usually 3 mm in diameter. This corresponds to a viscosity-pumping pressure relationship of 8 Pa s and 25 MPa, for example.) As the flow emerges from the mixing heads, the flow becomes laminar with phase separation (striation thickness) of about 10 μm . Reaction takes place at the interface during flow into the mold and subsequently in the mold until the products has sufficient strength to allow demolding.

The mixed liquids from the mixing head are forced (by pressure of liquid entering the mixing head) through a runner and gate and into the mold. It is generally required that the flow of the mixture should be laminar in the form of a film of about 1 mm thickness at a flow rate of about 2 m/s. Turbulent flow may cause air entrapment. The flow should be directed to the lower part of the mold to allow upward filling and any small amount of foaming to compensate for shrinkage (5%). The mold design should be such that air can escape through the parting lines.

Because of the low pressure (0.3 MPa) in the mold as compared to those encountered in thermoplastic injection molding (150 MPa) this process is suitable for the production of thin part with large surface areas. A significant application for this is in panel formation in the automotive industry, including fascias, door panels, spoilers, grills, and bumpers. While a rigid foam part with a flexural strength of 700 MPa would require a thickness of 7 mm, a RRIM part, because of the reinforcement, would allow a much smaller thickness (<3 mm) by virtue of the increase in flexural modulus.

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Commercial Polymer Blends and Alloys

The following index of trade names and suppliers is based on a choice of commercial polymer blends and alloys. No claim is made for completeness. Detailed lists can be found in the source cited.

Blend	Manufacturer	Composition	Reinforced ^a	Properties and Typical Uses
Alcryn	Du Pont	PO/EPDM	—	Processable, TPO
Arloy 1000	Arco Chem. Co.	PC/SMA	—	Automotive, medical
Arloy 2000	Arco Chem. Co.	SMA/PET	—	Food grade, transp.
Azloy	Azdel Inc.	PC/PBT	Yes	Automobile, electronics
Bayblend	Mobay/Bayer	PC/ABS	GF, Al	High impact strength, dimensional stability
Bexloy V	Du Pont	TPO blends	—	Automotive fascias
Bexloy W	Du Pont	Ionomeric alloys	—	Automotive bumper
Candon	Monsanto	SMA/ABS	—	Moldability, paintability
Celanex	Celanese	PBT/PET/Elast.	GF	Mechanical properties
Cycolac EHA	Borg-Warner	ABS/PC	—	Automotive applications
Cycoloy	Borg-Warner/Ube	ABS/PC or TPU	—	Heat, impact resistance
Cycoloy EHA	Borg-Warner	PC/ABS	—	Automotive applications
Denka HS	Denki Kagaku	ABS/PC	—	Automotive, electronic
Dia Alloy	Mitsubishi Rayon	ABS/PC	—	Automotive, electronics
Diacon	ICI	Acrylic/East.	—	Clear
Duraloy/Vandar	Celanese/Hoechst	POM/TPU or PBT	GF	Automotive, electronics
Durethan	Bayer AG	Nylon-6/PO or Elast.	—	Household appliances
Dynyl	Rohne-Poulenc	Nylon-6,6-modified block	GF	Low T impact, flex properties, sports goods
Ektar MB	Eastman Kodak	PCTG/PC or SMA	—	Electronic, appliances
Elemid	Borg-Warner	ABS/nylon	—	Auto, high T application
Envex	Rogers Corp.	PI/PTFE	—	Continuous-use $T=225^{\circ}\text{C}$

(continued)

Blend	Manufacturer	Composition	Reinforced ^a	Properties and Typical Uses
Estane	B. F. Goodrich	TRU/SAN	—	Chemical/oil resistance
ETA Polymer	Republic Plast.	PO/EPDM	—	Automotive application
FerroFlex	Ferro Corp.	PP/EPDM	—	Automotive, electric
Fulton KL	LNP Corp.	POM/PTFE (20%)	—	Moving parts, automotive
Gafite/Celanex	GAF Corp./Hoechst	PBT/Elastomer	GF, mica	Electronics
Geloy XP 4001	G.E.	ASN/PC	—	Automotive
Geloy XP 2003	G.E.	ASN/PVC	—	Sidings, impact strength
Geloy SCC 1320	G.E.	ASA/PMMA	—	Gloss, surface hardness
Gemax	G.E.	PPE/PBT	Yes	Automotive applications
Geon	B. F. Goodrich	PVC/NBR	—	Coating, binding
Grilamid	EMS-Chem.	Nylon-12 aromatic-aliphatic PA	—	Eye-glass frames
Grilon	EMS-Chem. AG	Nylon-6/Elastomer	GF ($\leq 30\%$)	Moldability, low T strength
Hostadur X	Hoechst AG	PBT/PET	GF	Computer, appliances
Hostaform	Hoechst AG	POM/TPU	MoS ₂ , PTFE	Impact strength
Hostalen	Hoechst AG	PP/EPDM	GF, talc	Automotive applications
Hostyren	Hoechst AG	PS/Elastomer	—	High impact PS
Hytrel	Du Pont	TPEs Elastomer	—	Blow molding
Idemitsu SC-250	Idemitsu Petrochem	PC/ABS,PES, Elastomer	—	Automotive, housings
Kelburon	DSM	PP/EPDM	—	Bumpers, suitcases
Keltan	DSM	PP/EPDM	—	Automotive parts
Koroseal	B. F. Goodrich	PVC/PVF	—	Linings
Kralastic	Uniroyal/Sumitomo	ABS/PVC	—	Moldability
Kraton D	Shell	SBS, SIS, SEP alloys	—	Automotive, sport
Kraton D2103	Shell	SBS/HIPS	—	Food containers
Kraton G	Shell	SEBS blends	—	Thermoplastic rubber
Krynac NV	Polysar Inc.	NBR/PVC (30–50%)	—	Weather, low T flex
Kydene	Rohm and Hass	PVC/PMMA	—	Thermoformable sheets
Kydex 100	Rohm and Hass	PVC/Acrylic	—	Thermoformable sheets
Lexan 100	G.E.	PC/PO	—	Electrical, housings
Lexan 500, 3000	G.E.	PC/PO	GF	Glass/metal replacement
Lomond	G.E.	PBT/SBS/ASA	—	Sporting, safety equip.
Luranyl	BASF	PPE/HIPS	GF, mineral	Housings, electronics
Makroblend PR	Bayer/Mobay	PC/PET or PBT	—	Bumpers
Makroblend	Bayer/Mobay	PBT/Elastomer	Yes	Automotive parts
Maranyl	ICI	Nylon-6 or 6,6/Elastomer	GF, mineral	Sport, automotive parts
Merlon	Bayer/Mobay	PC/PO	—	Toughened PC
Mertex	Mobay	TPU blends	—	
Metamable	Teijin	PC/PMMA	—	Decorative use
Mindel A	Amoco	PSO/ABS	—	Hot water resistance
Mindel B	Amoco	PSO/PET	GF (40%)	High heat resistance

(continued)

Blend	Manufacturer	Composition	Reinforced ^a	Properties and Typical Uses
Minlon	Du Pont	Nylon-6,6/ionomer	Mineral	Low-T impact strength
Nipeon AL	Zeon Kasei	ABS/PVC (50%)	—	Good weatherability
Nipol	Nippon	NBR/PVC (30%)	—	Fuel hoses
Noryl	G.E.	PPE/HIPS	Yes	Processability, impact
Noryl FN	G.E.	PPE/HIPS	Foamable	Equipment housing
Noryl GEN	G.E.	PEF/HIPS	GF	Continuous-use T = 100°C
Noryl GTX (Noryl Plus)	G.E.	PA/PPE (30%)	Yes	Auto panels, wheels, fenders
Novalloy	Daicel	ABS/PC	—	Automotive, electrical
Novamate A	Mitsubishi	AAS/PC	GF (15%)	Electrical, electronic
Novamate B	Mitsubishi	ABS/PC	—	Automotive application
Novarex AM	Mitsubishi	PC/Elastomer	—	Car instrument panels
Novelen KR	BASF	PP/EPR	—	Self-supporting bumpers
Nydur	Bayer/Mobay	Nylon/Elastomer	GF (15%)	Low-T impact strength
Orgalloy	Atochem	Nylon-6/PP	—	Automobile body. Underhood
Pellethane	Dow	ABS/PTU	—	Automobile bumpers
Pocan S	Mobay/Bayer	PBT/Elastomer	—	Automotive applications
Polycomp	LNP Corp.	PPS or PET/	CE, GF	Bearings, cams, gears
Polyman 506	A. Schulman	PVC/ABS	—	Housings, appliances
Polyman 552	A. Schulman	SAN/PO	—	Recreational applications
Polysar	Polysar Inc.	PS/PB (4–8%)	—	Food containers
Prevex	Borg-Warner	PPE copal./HIPS	GF ($\leq 30\%$)	Low-T impact strength
Pro-fax	Himont	PP/EPR	—	Automotive, houseware
Proloy	Borg-Warner	ABS/PC	—	Appliance housings
Propathane	ICI	PP/Elastomer	GF	Automotive applications
Pulse	Dow	PC/ABS (30%)	Yes	Auto panels, wheel covers
Rislan	Atochem	Nylon-6,6/PEBA	—	Sports goods
Riteflex BP	Hoechst Celanese	TPEs alloys	—	Golf carts, athletic shoes spoilers
Ronfalin	DSM	ABS/PC	—	Computer housings
Ronfalo V	DSM	ABS/PVC	—	Business machines
Rynite SST	Du Pont	PET/Elastomer	GF (35%)	Automotive body parts
Santoprene	Monsanto	PP/EPDM	—	Thermoplastic rubbers
Saranex	Dow	PVDC/PE	—	Film applications
Selar	Du Pont	PA/PO	—	Blow molding
Styron XL	Dow	PS/Elastomer	—	Electronic
Technyl A	Rhone-Poulenc	Nylon-6,6/elastomer	—	Auto, recreational
Technyl B	Rhone-Poulenc	Nylon-6,6/Elastomer	GF ($\leq 50\%$)	Mechanical and electrical properties

(continued)

Blend	Manufacturer	Composition	Reinforced ^a	Properties and Typical Uses
Telcar	Teknor Apex	PO/EPDM	—	Automotive application
Tenneco Terblend B	Tenneco Polymers	PVC/EVA	—	Building industry
Terblend S	BASF	ABS/PS	Low-T impact	
	BASF	ASA/PC	Yes	Auto, household applications
Texin	Mobay	PC/TPU	—	Thermoplastic rubber
Thermocomp PDX	LNP Corp.	PEEK/PTFE (20%)	—	Moving parts
Thermocomp	LNP Corp.	Nylon-6,6/Silicone	GF ($\leq 30\%$)	For injection molding
Torlon	Amoco	PAI/PTFE (3%)	Yes	Strength, thermal resistance
TPO 900	Reichold	PP/EPDM	—	Thermoplastic rubber
Triax 1120	Monsanto	Nylon-6/ABS	—	Impact heat, chemical resistance
Triax 2000	Monsanto	PC/ABS	—	Automotive market
Tribolon	Tribol. Ind. Inc.	PI/PTFE	—	Aerospace parts
Tribolon XT	Tribol. Ind. Inc.	PPS/PTFE	—	Moving parts
Tufrex VB	Mitsubishi Monsanto	ABS/PVC	—	Electronics housings
Ucardel P4174	G.E.	PSO/SAN	—	Single phase, transparent
Ultem	G.E.	PEI/PC	$\leq 40\%$	
Ultrablend KR	BASF	PBT or PET/PC/Elastomer	—	Bumpers, auto parts
Ultrablend S	BASF	PBT/ASA or SAN	GF ($\leq 30\%$)	Electronic, automotive
Ultramid/Terluran	BASF	Nylon/ABS	Mineral	Resistance to environmental stress cracking
Ultranyl	BASF	PPE/nylon	Yes	Automotive
Ultrason	BASF	PSO alloys	—	Electr., appliances
Valox 500 or 700	G.E.	PBT/PET or PBT/PC/Elastomer	GF ($\leq 45\%$)	Dimensional stability
Vandar 8001	Hoechst-Celanese	PBT blend	Yes	Exterior automotive body panels
Vectra	Celanese	LCP blends	—	High-T mechanical properties
Vestoblend	Hüls	Nylon/PPE	—	Automotive applications
Vestolen	Hüls	PP/EPDM	—	Automotive, sport
Vestoran	Hüls	HIPS/PPE/Elastomer	—	Automotive
Victrex VKT	ICI	PEEK/PTFE (7.5–30%)	—	Moving parts, bearings
Victrex VST	ICI	PES/PTFE	—	Bearing applications
Xenoy 1000	G.F	PC/PBT (50%)	Yes	Low-T properties, car bumpers
Xycon	Amoco	TPEs/TPU	—	Bumper beams, electr.
Xyron 200	Asahi Chem. Ind.	PPE/HIPS	—	Office equipment
Xyron A	Asahi Chem. Ind.	PPE/nylon	—	Electric, automotive
Zytel 300, 400	Du Pont	Nylon-6,6/Ionomer	—	Tubing, cables

^aCF, carbon fiber; GF, glass fiber.

Source: Utracki, L. A. 1989. Polymer Alloys and Blends: Thermodynamics and Rheology, Hanser Publishers, Munich/Vien-na/New York.

A14

Conversion of Units

SI Units and Conversion Factors

Physical Quantity	Name of SI Unit	Symbol for SI Unit	Definition of SI Unit
Length	Meter	m	Basic unit
Mass	Kilogram	kg	Basic unit
Time	Second	s	Basic unit
Force	Newton	N	kg m s^{-2} ($=\text{J m}^{-1}$)
Pressure	Pascal	Pa	$\text{kg m}^{-1} \text{s}^{-2}$ ($=\text{N m}^{-2}$)
Energy	Joule	J	$\text{kg m}^2 \text{s}^{-2}$
Power	Watt	W	$\text{kg m}^2 \text{s}^{-3}$ ($=\text{J s}^{-1}$)

Physical Quantity	Customary Unit	SI Unit	To Convert from Customary Unit to SI Units Multiply by
Length	in.	m	2.54×10^{-2}
Mass	lb	kg	4.5359237×10^{-1}
Force	dyne	N	1×10^{-5}
	kgf	N	9.80665
	lbf	N	4.44822
	dyne/cm ²	Pa or N/m ²	1×10^{-1}
Pressure	atm	Pa or N/m ²	1.01325×10^5
	mm Hg	Pa or N/m ²	1.33322×10^2
	lbf/in. ² or psi	Pa or N/m ²	6.89476×10^3
Energy	erg	J	1×10^{-7}
	Btu	J	1.055056×10^3
	ft.-lbf	J	1.35582
Area	in. ²	m ²	6.4516×10^{-4}
	ft. ²	M2	9.290304×10^{-2}
Density	lb/ft. ³	kg /m ³	1.6018463×10
Viscosity	poise	kg /(m.s)	1×10^{-1}
		or N s/m ²	

A15

Typical Properties of Polymers Used for Molding and Extrusion

	ASTM Test Method	Polyethylene		Polypropylene
		Low Density	High Density	
1. Specific gravity	D792	0.91–0.925	0.94–0.965	0.900–0.910
2. Tensile modulus (psi $\times 10^{-5}$)	D638	0.14–0.38	0.6–1.8	1.6–2.25
3. Compressive modulus (psi $\times 10^{-5}$)	D695	—	—	1.5–3.0
4. Flexural modulus (psi $\times 10^{-5}$)	D790	0.08–0.6	1.0–2.6	1.7–2.5
5. Tensile strength (psi $\times 10^{-3}$)	D638, D651	0.6–2.3	3.1–5.5	4.5–6.0
6. Elongation at break (%)	D638	90–800	20–130	100–600
7. Compressive strength (psi $\times 10^{-3}$)	D695	2.7–3.6	12–18	5.5–8.0
8. Flexural yield strength (psi $\times 10^{-3}$)	D790	—	1.0	6–8
9. Impact strength, notched Izod, (ft-lb/in.)	D256	No break	0.5–20	0.4–1.0
10. Hardness, Rockwell	D785	D40–51 (Shore)	D60–70 (Shore)	R80–102
11. Thermal conduct. (cal/s-cm-K $\times 10^4$)	C177	8.0	11–12	2.8
12. Specific heat (cal/g-K)	—	0.55	0.55	0.46
13. Linear therm. exp. coeff. (K $^{-1} \times 10^5$)	D696	10–22	11–13	8.1–10.0
14. Continuous-use temperature (°C)	—	80–100	120	120–160
15. Deflection temp. (°C at 0.45 MPa)	D648	38–49	60–88	107–121
16. Volume resistivity, ohm cm	D257	$> 10^{16}$	$> 10^{16}$	$> 10^{16}$
17. Dielectric constant at 1 kHz	D150	2.25–2.35	2.30–2.35	2.2–2.6
18. Dielectric strength (kV/in.)	D149	450–1000	450–500	500–660

(continued)

	ASTM Test Method	Polyethylene		Polypropylene
		Low Density	High Density	
19. Dissipation factor at 1 kHz	D150	<0.0005	<0.0005	<0.0018
20. Deleterious media	D543	Oxidizing acids	Oxidizing acids	Strong oxidizing acids
21. Solvents (room temperature) (Cl.H.=chlorinated hydrocarbons)		None	None	None

	ASTM Test Method	Polystyrene		Poly (methyl Methacrylate)
		Gen. Purpose	Impact-Resistant	
1. Specific gravity	D792	1.04–1.05	1.03–1.06	1.17–1.20
2. Tensile modulus (psi $\times 10^{-5}$)	D638	3.5–4.85	2.6–4.65	3.8
3. Compressive modulus (psi $\times 10^{-5}$)	D695	—	—	3.7–4.6
4. Flexural modulus (psi $\times 10^{-5}$)	D790	4.3–4.7	3.3–4.0	4.2–4.6
5. Tensile strength (psi $\times 10^{-3}$)	D638, D651	5.3–7.9	3.2–4.9	7–11
6. Elongation at break (%)	D638	1–2	13–50	2–10
7. Compressive strength (psi $\times 10^{-3}$)	D695	11.5–16	4–9	12–18
8. Flexural yield strength (psi $\times 10^{-3}$)	D790	8.7–14	5–12	13–19
9. Impact strength, notched Izod, (ft. lb/in.)	D256	0.25–0.40	0.5–11	0.3–0.5
10. Hardness, Rockwell	D785	M65–80	M20–80	M85–105
11. Thermal conduct. (cal/s-cm-K $\times 10^4$)	C177	2.4–3.3	1.0–3.0	4–6
12. Specific heat (cal/g-K)	—	0.32	0.32–0.35	0.35
13. Linear therm. exp. coeff. (K $^{-1} \times 10^5$)	D696	6–8	3.4–21	5–9
14. Continuous-use temperature (°C)	—	66–77	60–79	60–88
15. Deflection temp. (°C at 0.45 MPa)	D648	75–100	75–95	80–107

(continued)

	ASTM Test Method	Polystyrene		Poly (methyl Methacrylate)
		Gen. Purpose	Impact-Resistant	
16. Volume resistivity, ohm cm	D257	10^{16}	10^{16}	10^{14}
17. Dielectric constant at 1 kHz	D150	2.4–2.65	2.4–4.5	3.0–3.6
18. Dielectric strength (kV/in.)	D149	500–700	300–600	400
19. Dissipation factor at 1 kHz	D150	0.0001–0.0003	0.0004–0.002	0.03–0.05
20. Deleterious media	D543	Strong oxidizing acids	Strong Oxidizing acids	Strong bases and strong, oxidizing acids
21. Solvents (room temperature) (Cl.H. = chlorinated hydrocarbons)		Aromatic and Cl.H.	Aromatic and Cl.H.	Ketones, esters, aromatic, and Cl.H.

	ASTM Test Method	Poly(Vinyl Chloride)		
		Rigid	Plasticized	ABS Medium Impact
1. Specific gravity	D792	1.30–1.58	1.16–1.35	1.03–1.06
2. Tensile modulus ($\text{psi} \times 10^{-5}$)	D638	3.5–6	—	3–4
3. Compressive modulus ($\text{psi} \times 10^{-5}$)	D695	—	—	2.0–4.5
4. Flexural modulus ($\text{psi} \times 10^{-5}$)	D790	3–5	—	3.7–4.0
5. Tensile strength ($\text{psi} \times 10^{-3}$)	D638, D651	6–7.5	1.5–3.5	6–7.5
6. Elongation at break (%)	D638	2–80	200–450	5–25
7. Compressive strength ($\text{psi} \times 10^{-3}$)	D695	8–13	0.9–1.7	10.5–12.5
8. Flexural yield strength ($\text{psi} \times 10^{-3}$)	D790	10–16	—	11–13
9. Impact strength, notched Izod, (ft-lb/in.)	D256	0.4–20	—	11–13
10. Hardness, Rockwell	D785	D65-85(Shore)	A40-100(Shore)	R107-115
11. Thermal conduct. ($\text{cal/s-cm-K} \times 10^4$)	C177	3.5–5.0	3.0–4.0	4.5–8.0
12. Specific heat (cal/g-K)	—	0.2–0.28	0.3–0.5	0.3–0.4

(continued)

	ASTM Test Method	Poly(Vinyl Chloride)		
		Rigid	Plasticized	ABS Medium Impact
13. Linear therm. exp. coeff. ($K^{-1} \times 10^5$)	D696	5–10	7–25	8–10
14. Continuous-use temperature ($^{\circ}C$)	—	65–80	65–80	71–93
15. Deflection temp. ($^{\circ}C$ at 0.45 MPa)	D648	57–82	—	102–107
16. Volume resistivity, ohm cm	D257	$> 10^{16}$	10^{11} – 10^{15}	2.7×10^{16}
17. Dielectric constant at 1 kHz	D150	3.0–3.3	4–8	2.4–4.5
18. Dielectric strength (kV/in.)	D149	425–1300	300–1000	350–500
19. Dissipation factor at 1 kHz	D150	0.009–0.017	0.07–0.16	0.004–0.007
20. Deleterious media	D543	None	None	Conc. oxidizing acids, organic solvents
21. Solvents (room temperature) (Cl.H.=chlorinated hydrocarbons)		Ketones, esters, swelling in aromatic, and Cl. H.	Plasticizer may be extracted. Otherwise like rigid PVC	Ketones, esters, some Cl.H.

	ASTM Test Method	Cellulose Acetate	Cellulose Acetate Butyrate	Fluoropolymers	
				$-\text{CF}_2-\text{CF}_2-$	$-\text{CF}_2-\text{CHCl}-$
1. Specific gravity	D792	1.22–1.34	1.15–1.22	2.14–2.20	2.1–2.2
2. Tensile modulus ($\text{psi} \times 10^{-5}$)	D638	0.65–4.0	0.5–2.0	0.58	1.5–3.0
3. Compressive modulus ($\text{psi} \times 10^{-5}$)	D695	—	—	—	—
4. Flexural modulus ($\text{psi} \times 10^{-5}$)	D790	—	—	—	—
5. Tensile strength ($\text{psi} \times 10^{-3}$)	D638, D651	1.9–9.0	2.6–6.9	2–5	4.5–6.0
6. Elongation at break (%)	D638	6–70	40–88	200–400	80–250
7. Compressive strength ($\text{psi} \times 10^{-3}$)	D695	3–8	2.1–7.5	1.7	4.6–7.4
8. Flexural yield strength ($\text{psi} \times 10^{-3}$)	D790	2–16	1.8–9.3	—	7.4–9.3
9. Impact strength, notched Izod, (ft-lb/in.)	D256	1–7.8	1–11	3.0	2.5–2.7

(continued)

	ASTM Test Method	Cellulose Acetate	Cellulose Acetate Butyrate	Fluoropolymers	
				—CF ₂ —CF ₂ —	—CF ₂ —CHCl—
10. Hardness, Rockwell	D785	R34-125	R31-116	D50-55(Shore)	R75-95
11. Thermal conduct. (cal/s-cm-K × 10 ⁴)	C177	4–8	4–8	6.0	4.7–5.3
12. Specific heat (cal/g-K)	—	0.0–0.4	0.3–0.4	0.25	0.22
13. Linear therm. exp. coeff. (K ⁻¹ × 10 ⁵)	D696	8–18	11–17	10	4.5–7.0
14. Continuous-use temperature (°C)	—	60–105	60–105	290	175–200
15. Deflection temp. (°C at 0.45 MPa)	D648	50–100	54–108	121	126
16. Volume resistivity, ohm cm	D257	10 ¹⁰ –10 ¹⁴	10 ¹¹ –10 ¹⁵	10 ¹⁸	1.2 × 10 ¹⁸
17. Dielectric constant at 1 kHz	D150	3.4–7.0	3.4–6.4	2.1	2.3–2.7
18. Dielectric strength (kV/in.)	D149	250–500	250–400	480	500–600
19. Dissipation factor at 1 kHz	D150	0.01–0.07	0.01–0.04	0.002	0.023–0.027
20. Deleterious media	D543	Strong acids and bases	Strong acids and bases	None	None
21. Solvents (room temperature) (Cl.H. = chlorinated hydrocarbons)		Ketones, esters, Cl.H	Ketones, esters, Cl.H	None	Swells in Cl.H.

	ASTM Test Method	Nylon-6,6 (Moisture Conditioned)	Nylon-6 (Moisture Conditioned)	Acetal	Polycarbonate
1. Specific gravity	D792	1.13–1.15	1.12–1.14	1.42	1.2
2. Tensile modulus (psi × 10 ⁻⁵)	D638	—	1.0	5.2	3.5
3. Compressive modulus (psi × 10 ⁻⁵)	D695	—	2.5	6.7	3.5
4. Flexural modulus (psi × 10 ⁻⁵)	D790	1.75–4.1	1.4	3.8–4.3	3.4

(continued)

	ASTM Test Method	Nylon-6,6 (Moisture Conditioned)	Nylon-6 (Moisture Conditioned)	Acetal	Polycarbonate
5. Tensile strength (psi $\times 10^{-3}$)	D638, D651	11	10	9.5–12	9.5
6. Elongation at break (%)	D638	300	300	25–75	110
7. Compressive strength (psi $\times 10^{-3}$)	D695	—	—	18	12.5
8. Flexural yield strength (psi $\times 10^{-3}$)	D790	6.1	5.0	14	13.5
9. Impact strength, notched Izod, (ft-lb/in.)	D256	2.1	3.0	1.3–2.3	16
10. Hardness, Rockwell	D785	R120	R119	M94 to R120	M70
11. Thermal conduct. (cal/s-cm-K $\times 10^4$)	C177	5.8	5.8	5.5	4.7
12. Specific heat (cal/g-K)	—	0.4	0.38	0.35	0.3
13. Linear therm. exp. coeff. (K $^{-1} \times 10^5$)	D696	8.0	8.0–8.3	10	6.8
14. Continuous-use temperature (°C)	—	80–150	80–120	90	121
15. Deflection temp. (°C at 0.45 MPa)	D648	180–240	150–185	124	138
16. Volume resistivity, ohm cm	D257	10 ¹⁴ –10 ¹⁵	10 ¹² –10 ¹⁵	1.0 $\times 10^{15}$	2 $\times 10^{16}$
17. Dielectric constant at 1 kHz	D150	3.9–4.5	4.0–4.9	3.7	3.02
18. Dielectric strength (kV/in.)	D149	385–470	440–510	500	400
19. Dissipation factor at 1 kHz	D150	0.02–0.04	0.011–0.06	0.004	0.0021
20. Deleterious media	D543	Strong acids	Strong acids	Strong acids, some other acids and bases	Bases and strong acids
21. Solvents (room temperature) (Cl.H. = chlorinated hydrocarbons)		Phenol and formic acid	Phenol and formic acid	None	Aromatic and Cl.H.

	ASTM Test Method	Ionomers	Poly(Phenylene Oxide)	Polysulfone
1. Specific gravity	D792	0.93–0.96	1.06	1.24
2. Tensile modulus (psi $\times 10^{-5}$)	D638	0.2–0.6	3.55	3.6
3. Compressive modulus (psi $\times 10^{-5}$)	D695	—	—	3.7
4. Flexural modulus (psi $\times 10^{-5}$)	D790	—	3.6–4.0	3.9
5. Tensile strength (psi $\times 10^{-3}$)	D638, D651	3.5–5.0	9.6	10.2 (yield)
6. Elongation at break (%)	D638	350–450	60	50–100
7. Compressive strength (psi $\times 10^{-3}$)	D695	—	16.4	13.9 (yield)
8. Flexural yield strength (psi $\times 10^{-3}$)	D790	—	13.5	15.4 (yield)
9. Impact strength, notched Izod, (ft-lb/in.)	D256	6.0–15	5.0	1.2
10. Hardness, Rockwell	D785	D50–65 (Shore)	R119	M69, R120
11. Thermal conduct. (cal/s-cm-K $\times 10^4$)	C177	5.8	5.2	2.8
12. Specific heat (cal/g-K)	—	0.55	—	0.31
13. Linear therm. exp. coeff. (K $^{-1} \times 10^5$)	D696	12	3.3–5.9	5.2–5.6
14. Continuous-use temperature (°C)	—	70–95	—	150–175
15. Deflection temp. (°C at 0.45 MPa)	D648	38	—	180
16. Volume resistivity, ohm cm	D257	$> 10^{16}$	10^{18}	5×10^{16}
17. Dielectric constant at 1 kHz	D150	2.4	2.6	3.13
18. Dielectric strength (kV/in.)	D149	900–1100	400–500	425
19. Dissipation factor at 1 kHz	D150	0.0015	0.00035	0.001
20. Deleterious media	D543	Acids, esp. strong Oxidizing acids	None	None
21. Solvents (room temperature) (Cl.H. = chlorinated hydrocarbons)		None	Aromatic and Cl.H.	Aromatic hydrocarbons

	ASTM Test Method	Phenol– Formaldehyde (Cellulose Fill)	Melamine– Formaldehyde (Cellulose Fill)	Cast Epoxy Glass Fiber Fill
1. Specific gravity	D792	1.37–1.46	1.47–1.52	1.6–2.0
2. Tensile modulus (psi $\times 10^{-5}$)	D638	8–17	11–14	30
3. Compressive modulus (psi $\times 10^{-5}$)	D695	—	—	—
4. Flexural modulus (psi $\times 10^{-5}$)	D790	10–12	—	20–45

(continued)

	ASTM Test Method	Phenol- Formaldehyde (Cellulose Fill)	Melamine- Formaldehyde (Cellulose Fill)	Cast Epoxy Glass Fiber Fill
5. Tensile strength (psi $\times 10^{-3}$)	D638, D651	5-9	5-13	5-20
6. Elongation at break (%)	D638	0.4-0.8	0.6-1.0	4
7. Compressive strength (psi $\times 10^{-3}$)	D695	25-31	33-45	18-40
8. Flexural yield strength (psi $\times 10^{-3}$)	D790	7-14	9-16	8-30
9. Impact strength, notched Izod, (ft.lb/in.)	D256	0.2-0.6	0.2-0.4	0.3-10
10. Hardness, Rockwell	D785	E64-95	M115-125	M100-112
11. Thermal conduct. (cal/s-cm-K $\times 10^4$)	C177	4-8	6.5-10	4-10
12. Specific heat (cal/g-K)	—	0.35-0.40	0.4	0.19
13. Linear therm. exp. coeff. (K $^{-1} \times 10^5$)	D696	3.0-4.5	4.0-4.5	1-5
14. Continuous-use temperature (°C)	—	150-175	99	150-260
15. Deflection temp. (°C at 0.45 MPa)	D648	—	43	—
16. Volume resistivity, ohm cm	D257	10^9-10^{13}	10^{12}	$> 10^{14}$
17. Dielectric constant at 1 kHz	D150	4.4-9.0	7.8-9.2	3.5-5.0
18. Dielectric strength (kV/in.)	D149	200-400	270-300	300-400
19. Dissipation factor at 1 kHz	D150	0.04-0.20	0.015-0.036	0.01
20. Deleterious media	D543	Strong bases and oxidizing acids	Strong acids and bases	None
21. Solvents (room temperature) (Cl.H. = chlorinated hydrocarbons)		None	None	None

Conversion Factors: 1000 psi = 6.895 MPa; 1 ft.lb/in. = 53.4 J/m; 1 cal = 4.187 J; 1 kV/in. = 0.0394 MV/m, data collected from *Modern Plastics Encyclopedia*

A16

Typical Properties of Cross-Linked Rubber Compounds

A. Diene-Based Polymers and Copolymers

	Styrene–Butadiene Random Copolymer, 25% (wt) Styrene (SBR)	Styrene–Butadiene Block Copolymer, about 25% Styrene (YSBR)	Cis-1,4- Polyisoprene (Natural Rubber NR, Also Made Synthetically IR)	Cis-1,4 Polybutadiene (BR)	Polychloroprene (CR), Neoprene	Butadiene– Acrylonitrile Random Copolymer, Variable % Acrylonitrile (NBR)	Reclaimed Rubber (Whole Tires) (Mainly NR and SBR)
<i>Gum stock (cross-linked, Unfilled)</i>							
Density (g/cm ³)	0.94	0.94–1.03	0.93	0.93	1.23	1.00	1.2 (compd'd)
Tensile strength (psi) ^a	200–400	1700–3700	2500–3000	200–1000	3000–4000	500–1000	
Resistivity (ohm cm, log)	15	13	15–17	—	11	10	
Dielect. const. at 1 kHz	3.0	3.4	2.3–3.0	2.3–3.0	9.0	13	
Dielect. str. (kV/in.) ^b	—	485	—	—	150–600		
Diss. factor, at 1 kHz	0.003	0.01	0.002–0.003	0.002–0.003	0.03	0.055	
Reinforced stock							
Tensile strength (psi) ^a	2000–3500	1000–3000	3000–4000	2000–3500	3000–4000	3000–4000	500–1000
Elong. at break (%)	300–700	500–1000	300–700	300–700	300–700	300–700	300–400
Hardness, Shore A	40–100	40–85	20–100	30–100	20–100	30–100	50–100
Cont. high-temp. limit (°C)	110	65	100	100	120	120	100
Stiffening temp. (°C)	–20 to –45	–50 to –60	–30 to –45	–35 to –50	–10 to –30	0 to –30	–20 to –45
Brittle temp. (°C)	–60	–70	–60	–70	–40 to –55	–15 to –55	–60
Resilience	Good	Excellent	Excellent	Excellent	Good	Fair	Good
Resistance to							
Acid	Good	Good	Good	Good	Good	Good	Good
Alkali	Good	Good	Good	Good	Good	Good	Good
Gasoline and oil	Poor	Poor	Poor	Poor	Good	Excellent	Poor
Aromatic hydrocarbons	Poor	Poor	Poor	Poor	Fair	Good	Poor
Ketones	Good	Poor	Good	Good	Poor	Poor	Good
Chlorinated solvents	Poor	Poor	Poor	Poor	Poor	Poor	Poor
Oxidation	Good	Good	Good	Good	Excellent	Fair	Good
Ozone	Good	Good	Good	Good	Poor	Fair	Good

Abbreviations are according to ASTM.

^a 1000 psi = 6.895 MPa.

^b 1 kV/in. = 0.0394 MV/m.

B. Saturated, Carbon-chain Polymers

	Polyisobutylene (Butyl Rubber, Copolymer with 0.5–2% Isoprene) (IIR)	Chloro-Sulfonated Polyethylene (CSM)	Ethylene–Propylene Random Copolymer, 50% Ethylene (EPM)	Ethylene–Propylene Random Terpolymer 50% Ethylene (EPDM)	Poly(Ethyl Acrylate), Usually a Copolymer (ACM)	Vinylidene– Fluoride– Chlorotrifluoro Ethylene Random Copolymer (FKM)	Vinylidene– Fluoride– Hexafluoropropylene Random Copolymer (FKM)
<i>Gum stock (cross-linked, unfilled)</i>							
Density (g/cm ³)	0.92	1.12–1.28	0.86	0.86	1.10	1.85	1.85
Tensile strength (psi) ^a	2500–3000	2500	500	200	200–400	200–2500	2000
Resistivity (ohm cm, log)	17	14	16	16	—	14	13
Dielect. const. at 1 kHz	2.1–2.4	7–10	3.0–3.5	3.0–3.5	—	6	—
Dielect. str. (kV/in.) ^b	600	500	900	900	—	600	250–750
Diss. factor, at 1 kHz	0.003	0.03–0.07	0.004–0.008	0.004–0.008	—	0.05	0.03–0.04
<i>Reinforced stock</i>							
Tensile strength (psi) ^a	2000–3000	3000	1000–3000	1000–3500	1500–2500	1500–2500	1500–2500
Elong. at break (%)	300–700	300–500	200–300	200–300	250–350	300–400	300–400
Hardness, Shore A	30–100	50–100	30–100	30–100	40–100	50–90	50–90
Cont. high-temp. limit (°C)	120	160	150	150	175	200	250
Stiffening temp. (°C)	–25 to –45	–10 to –30	–40	–40	—	–35	—
Brittle temp. (°C)	–60	–40 to –55	–50 to –75	–50 to –75	–30	–50	–45
Resilience	Fair	Good	Good	Good	Fair	Fair	Fair
<i>Resistance to</i>							
Acid	Excellent	Good	Excellent	Excellent	Fair	Excellent	Excellent
Alkali	Excellent	Good	Excellent	Excellent	Poor	Good	Good
Gasoline and oil	Poor	Good	Poor	Poor	Good	Excellent	Excellent
Aromatic hydrocarbons	Poor	Fair	Fair	Fair	Good	Good	Excellent
Ketones	Excellent	Poor	Good	Good	Poor	Poor	Poor
Chlorinated solvents	Poor	Poor	Poor	Poor	Poor	Good	Good
Oxidation	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Excellent
Ozone	Excellent	Excellent	Excellent	Excellent	Excellent	Good	Excellent

Abbreviations are according to ASTM.

^a 1000 psi = 6.895 MPa.^b 1 kV/in. = 0.0394 MV/m.

C. Heterochain Polymers

	Poly(Dimethyl Siloxane) Silicone Rubber, Usually Copolymer with Vinyl groups (VMQ)	Poly(Dimethyl Siloxane) Copolymer with Phenyl- Bearing Siloxane and Vinyl Groups (PVMQ)	Room Temperature Vulcanizing Silicone	Polysulfide (ET and EOT)	Polyurethane (AU and EU)
<i>Gum stock (cross-linked, unfilled)</i>					
Density (g/cm ³)	0.98	0.98	1.0–1.3 (compd'd)	1.35	1.25
Tensile strength (psi) ^a	50–100	50–100	—	100–200	2000–4000
Resistivity (ohm cm, log)	11–17	11–17	15	12	11–14
Dielect. const. at 1 kHz	3.0–3.5	3.0–3.5	2.8	7–9.5	5–8
Dielect. str. (kV/in.) ^b	100–600	100–600	500	250–600	350–525
Diss. factor, at 1 kHz	0.001–0.010	0.001–0.010	0.003	0.001–0.005	0.02–0.09
<i>Reinforced stock</i>					
Tensile strength (psi) ^a	500–1200	500–1500	400–800	1300–1800	3000–10,000
Elong. at break (%)	200–700	200–700	100–200	200–500	200–600
Hardness, Shore A	30–80	30–80	30–50	25–85	20–100
Cont. high-temp. limit (°C)	250	300	200–250	120	120
Stiffening temp. (°C)	–50	–100	–50 to –100	–25	–25 to –35
Brittle temp. (°C)	–50	–120	–50 to –100	–50	–50 to –60
Resilience	Fair	Fair	Fair	Fair	Poor
<i>Resistance to</i>					
Acid	Fair	Fair	Fair	Fair	Fair
Alkali	Fair	Fair	Fair	Good	Poor to fair
Gasoline and oil	Poor	Poor	Poor	Excellent	Excellent
Aromatic hydrocarbons	Poor	Poor	Poor	Good	Good
Ketones	Excellent	Excellent	Excellent	Good	Poor
Chlorinated solvents	Poor	Poor	Poor	Good	Poor
Oxidation	Excellent	Excellent	Excellent	Excellent	Excellent
Ozone	Excellent	Excellent	Excellent	Excellent	Excellent

Abbreviations are according to ASTM.

^a 1000 psi = 6.895 MPa.

^b 1 kV/in. = 0.0394 MV/m.

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Typical Properties of Representative Textile Fibers

Typical Properties of Representative Textile Fibers

Fiber/Chemical Name	Specific Gravity	Breaking Tenacity ^a (g/denier)		Elongation at Break (%)		Water Absorbed at 70°F, 65% rel. Humidity (%)	Thermal Stability
		Standard	Wet	Standard	Wet		
1. Acetate/cellulose acetate							
(a) Diacetate	1.32	1.2–1.4	0.8–1.0	25–45	35–50	6.4	(a) Sticks at 175–205°C; softens, 205–230°C; Melts, 260°C
(b) Triacetate	1.3	1.1–1.3	0.8–1.0	26–40	30–40	3.2	(b) Melts at 300°C
2. Acrylic/polyacrylonitrile	1.17	2.0–2.7	1.6–2.2	34–50	34–60	1.5	Shrinks 5% at 253°C
3. Aramid/aromatic polyamide							
(a) Kevlar (Du Pont)	1.44	21.7	21.7	2.5–4	2.5–4	4.5–7	(a) Decomposes at 500°C
(b) Nomex (Du Pont)	1.38	4.0–5.3	3.0–4.1	22–32	20–30	6.5	(b) Decomposes at 370°C
4. Cotton/ α -cellulose	1.54	3.0–4.9	3.0–5.4	3–10		7–8.5	Decomposes at 150°C
5. Fluorocarbon/poly(tetra-fluoroethylene)	2.1	0.9–2.0	0.9–2.0	19–140	19–140	Nil	Melts at about 288°C
6. Glass/silica, silicates	2.49–2.55	9.6–19.9	6.7–19.9	3.1–5.3	2.2–5.3	Nil	Softens at 730–850°C; does not burn
7. Nylon/aliphatic polyamide							
(a) Nylon-6	1.14	4.0–9.0	3.7–8.2	16–50	19–47	2.8–5.0	(a) Melts at 216°C; decomposes, 315°C
(b) Nylon-6,6	1.14	3.0–9.5	2.6–8.0	16–66	18–70	4.2–4.5	(b) Sticks at 230°C melts, 250–260°C
8. Olefin							
(a) Polyethylene (branched)	0.92	1.0–3.0	1.0–3.0	20–80	20–80	Nil	(a) Softens 105–115°C; melts 110–120°C; shrinks 5% at 75°C
(b) Polyethylene (linear)	0.95	3.5–7.0	3.5–7.0	10–45	10–45	Nil	(b) Softens 115–125°C; melts 125–138°C; Shrinks 5% at 75–80°C
(c) Polypropylene	0.90	3.0–8.0	3.0–8.0	14–80	14–80	0.01–0.1	(c) Softens 140–175°C; melts 160–177°C; shrinks 5% at 100–130°C
9. Polyester/poly(ethylene terephthalate)	1.38	2.2–9.5	2.2–9.5	12–55	12–55	0.4–0.8	Sticks at 230°C; melts, 250°C
10. Spandex/segmented polyurethane	1.21	0.7–0.9	—	400–625	—	1.3	Sticks at 215°C
11. Viscose rayon/regenerated cellulose							
(a) Regular	1.46–1.54	0.7–3.2	0.7–1.8	15–30	20–40	11–13	(a) Loses strength at 150°C
(b) High tenacity		3.0–5.7	1.9–4.3	9–26	14–34	—	(b) Decomposes at 175–240°C
12. Wool/protein	1.32	1.0–2.0	0.8–1.8	20–40		11–17	Decomposes at 130°C

^a Tensile strength (MPa) = tenacity (g/denier) \times density (g/cm³) \times 88.3.

Source: *Textile World*, 128(8), 57, 1978.